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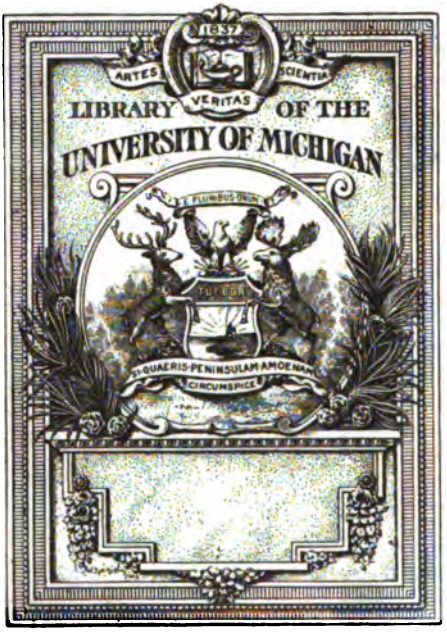

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TRANSACTIONS

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VOLUME XIV

Containing the Papers Read at the Meeting Held at Chicago, Ill., March 4th, 5th and 6th, 1912, Together with Supplementary Discussions and Other Matter.

HOMER F. STALEY, *Editor*

This Society is not, as an organization, responsible for the statements of facts or opinions expressed in these papers and discussions.

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SHOEMAKER, GEORGE W., 85 N. High St., Columbus, Ohio.	The Ohio Face Brick Company.
SIMPKINS, RALPH, St. Louis, Mo.	Manager, Hydraulic Pressed Brick Company.
SINCLAIR, HERBERT, Trenton, N. J.	General Manager, Star Porcelain Company.
SINGER, L. P., Lincoln, Cal.	Chemist, Gladding, McBean & Company.
SMITH, ALBERT E., Trenton, N. J.	Foreman, Electric Porcelain Company.

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SMITH, AMEDEE M., 1402 Yeon Bldg., Portland, Oregon.	
SMITH, DAVID CARLTON, Trenton, N. J.	Superintendent, Experimental Department, Trenton Potteries Company.
SMITH, HARRY W., 314 Smith St., East Liverpool, Ohio.	Representative, Roessler & Hasslacher Chemical Company.
SMITH, MORGAN BABCOCK, A.B., Syracuse, N. Y.	Chemist, The Solvay Process Company.
SMITH, NORMAN G., Auburn, Me.	Treasurer and General Manager, Maine Feldspar Company.
SMITH, PERRY A., New Brighton, Pa.	Secretary, A. F. Smith Company.
SOLON, ALBERT L., General Delivery, National City, Cal.	
SPEIR, HARRY F., Lewistown, Pa.	Superintendent, Pennsylvania Pulverizing Company.
SPIKER, JOHN A., Salt Lake City, Utah.	General Manager, Western Clay Products Company.
SPRINGE, OTTO, Galesburg, Ill.	Purington Paving Brick Company.
SPROAT, IRA E., 1505 W. 2d St., Dayton, O.	Chemist, Dayton Grinding Wheel Company.
STAMM, JOHN, 859 Ohio Ave., E. Liverpool, O.	Supt., The Croxall Chemical & Supply Company.
STANGL, MARTIN, CR., Flemington, N. J.	Superintendent, Technical Department, Fulper Pottery Company.
STAUDT, AUGUST, Perth Amboy, N. J.	Treasurer and General Manager, Ostegaard Tile Works.
STEVENSON, HUGH, Ellerslie, Md.	Superintendent, Andrew Ramsay Corporation.
STEVENSON, WILLIAM G., East Liverpool, Ohio.	General Manager, Ohio Silica Company.
STOUT, WILBER, 217 E. Mithoff Ave., Columbus, O.	Chemist, Columbus Iron & Steel Company.
STOWE, CHARLES BROWN, Cleveland, Ohio.	President, National Fire Brick Company.
STULL, RAY THOS., E.M. (in Cer.), Urbana, Ill.	Assistant Professor of Ceramics, University of Illinois.
SWALM, PHAON H., Trenton, N. J.	Assistant Superintendent, Trenton Fire Clay & Porcelain Company.
TAYLOR, WILLLIAM WATTS, Cincinnati, Ohio.	President, Rookwood Pottery Company.
TEETOR, PAUL, 40th and Butler Sts., Pittsburgh, Pa.	Laboratory Ass't Ceramic Chemist, Bureau of Standards.

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TEIPER, JOHN EDWARD, 195 Richmond Ave., Buffalo, N. Y.	Superintendent, Jewettville Brick Company.
THOMAS, CHAUNCEY RAPELJE, Deerfield, Mass.	Deerfield Pottery.
THOMAS, DAVID C., Minerva, Ohio.	Ceramic Chemist and Head Burner, Owen China Company.
THOMAS, GEORGE E., St. Louis, Mo.	General Superintendent, Highlands Fire Clay Company.
THOMAS, GEORGE W., East Liverpool, Ohio.	President and General Manager, The R. Thomas & Sons Company.
THRALL, CHARLES U., Tottenville, S. I., N. Y.	Superintendent, Atlantic Terra Cotta Company.
TILLOTSON, E. W., JR., B.A., PH.D., Lawrence, Kansas.	University of Kansas.
TIMMERMAN, WALTER F., Kansas City, Kansas.	Superintendent, Western Terra Cotta Company.
TONE, FRANK J., Niagara Falls, N. Y.	Works Manager, Carborundum Company.
TOWNSEND, EVERETT, 344 Bellevue Ave., Trenton, N. J.	General Manager, Robertson Art Tile Company.
TRUMAN, GAIL R., 5801 Manchester Ave., St. Louis, Mo.	Ceramic Chemist, St. Louis Terra Cotta Company.
TURNER, A. M., M.E., Sciotoville, O.	Superintendent and Treasurer, Scioto Fire Brick Company.
VODREY, WILLIAM E., East Liverpool, Ohio.	General Manager, Vodrey Pottery Company.
VOLLKOMMER, JOSEF, Empire Bldg., Pittsburgh, Pa.	President and Manager, The Vitro Manufacturing Company.
VOLZ, WILLIAM J., St. Louis, Mo.	Superintendent, Evens & Howard Fire Brick Company.
WAGNER, FRITZ, 1000 Clybourn Ave., Chicago, Ill.	Vice-President and Treasurer, The Northwestern Terra Cotta Company.
WALKER, CHARLES HENRY, 401 Vine St,. East Liverpool, Ohio.	Assistant Superintendent, Homer Laughlin China Company.
WALKER, F. WM., JR., B.S. (in M.E.), Beaver Falls, Pa.	Student, University of Illinois.
WALLACE, FRANK M., 77 West Main St., Chicago Heights, Ill.	Student, Ceramic Department, University of Illinois.
WALTON, SAMUEL FORMAN, Station A, Ames, Iowa.	Student in Ceramics, Iowa State College.
WANKA, F. O., Stockton, Cal.	Manager, Stockton Fire and Enamel Brick Company.
WARD, J. W., 628 E. Main St., Latrobe, Pa.	Assistant Superintendent, Pittsburgh High Voltage Insulator Company.

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WEITH, ARCHIE J., 1308 Ohio St., Lawrence, Kans.	Department of Industrial Research, University of Kansas.
WELLS, HARRY B., Charleston, W. Va.	Superintendent, West Virginia Clay Products Company.
WHEAT, HOWARD I., Allentown, Pa.	Superintendent, Allentown Paving Brick Plant.
WHITAKER, FREDERICK ALBERT, Keasbey, N. J.	Assistant Superintendent, German-American Stoneware Works.
WHITEHEAD, C. LOUIS, Box 153, Trenton, N. J.	President, Providential Tile Company.
WHITMER, J. D., CR.E., 9 Ball St., Zanesville, O.	American Encaustic Tile Company.
WHITTAKER, JOHN L., East Boston, Mass.	Superintendent, New England Pottery Company.
WILDER, THOMAS MILTON, Ravinia, Ill.	Proprietor, Wildwood Shop.
WILL, OTTO W., Perth Amboy, N. J.	Superintendent, Color Department, Roessler & Hasslacher Chemical Company.
WILLIAMS, ARTHUR E., 121 S. Fifth St., Monmouth, Ill.	Monmouth Brick & Tile Company.
WILLIAMS, IRA A., M.Sc., Ames, Iowa.	Associate Professor, Geology and Mining Engineering, Iowa State College.
WILLIAMS, WARREN STEPHEN, B.S., 1316 Bellefontaine St., Kansas City, Mo.	Kansas City Terra Cotta Company.
WORTH, S. HARRY, 706 Franklin Bank Building, Philadelphia, Pa.	President, Pennsylvania Feldspar Company.
YATES, ALFRED, Shawmut, Elk Co., Pa.	General Manager, Shawmut Paving Brick Company.
YOUNG, GEORGE F., Zanesville, Ohio.	Manager, Roseville Pottery Company.
YOUNG, SAMUEL ECCLES, C.E., 3451 California Ave., N. S., Pittsburg, Pa.	Aid, Bureau of Standards.
YOWELL, JOHN BENNETT, Dudley, Ill.	
ZOPFI, ALBERT S., Toledo, Ohio.	Secretary and Treasurer, Buckeye Clay Pot Company.

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GEOGRAPHICAL DISTRIBUTION OF MEMBERSHIP

Foreign Active Members

Canada	1	Germany	4

Resident Active Members

Alabama	1	New York	10
Illinois	1	Ohio	10
Indiana	1	Oregon	2
Maryland	1	Pennsylvania	13
Massachusetts	1	Washington	1
Michigan	1	West Virginia	1
Missouri	4	Virginia	1
New Jersey	6		

Foreign Associate Members

Australia	1	Mexico	1
Canada	8	New Zealand	1
England	8	Scotland	1
France	2	Sicily	1
Germany	2	Spain	1
Hungary	1	Sweden	1
Japan	5		

Resident Associate Members

Alabama	3	Mississippi	1
California	8	Missouri	14
Colorado	5	Montana	2
Connecticut	1	New Hampshire	1
Delaware	1	New Jersey	54
District of Columbia	1	New York	37
Georgia	2	North Carolina	1
Illinois	35	Ohio	90
Indiana	5	Oklahoma	1
Iowa	6	Oregon	1
Kansas	7	Pennsylvania	37
Kentucky	4	Utah	5
Maryland	7	Washington	11
Maine	1	West Virginia	3
Massachusetts	15	Wisconsin	3
Michigan	1	Wyoming	1

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RULES OF THE SOCIETY.

(Revised 1911.)

I.

OBJECTS.

The objects of the American Ceramic Society are to promote the arts and sciences connected with ceramics by means of meetings for the reading and discussion of professional papers, the publication of professional literature, and for social intercourse.

II.

MEMBERSHIP.

The Society shall consist of Honorary Members, Active Members, Associate Members and Contributing Members.

Honorary Members must be persons of acknowledged professional eminence, whom the Society wishes to honor in recognition of their achievements in ceramic science or art. Their number shall at no time exceed two per cent. of the combined active and associate membership.

Active Members must be persons competent to fill responsible positions in ceramics. Only Associate Members shall be eligible to election as Active Members, and such election shall occur only in recognition of attainments in the field of ceramics, and interest in the Society, as evidenced by papers or discussions contributed to its meetings.

Associate Members must be persons interested in ceramics or allied arts.

Contributing Members must be persons, firms, or corporations who, being interested in the Society, make such financial contributions for its support as are prescribed in Section 3.

Honorary Members shall be nominated for election by at least five active members, and approved by the Board of Trustees. Their nomination shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of at least 90 per cent. of those voting, by letter ballot, at the next succeeding annual meeting.

To be promoted to active membership, Associate Members must be nominated in writing by an Active Member, and must be seconded by not less than two other Active Members, and must be approved by the Board of Trustees. Their nomination shall be accompanied by a statement of their professional qualifications and a list of their publications, if any. Their nominations, when approved by the Board of Trustees, shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of not less than 75 per cent. of those voting, by letter ballot, at the next succeeding annual meeting.

A candidate for Associate Membership must make application upon a form, prepared by the Board of Trustees, which shall contain a written statement of the age and professional experience of the candidate, and a pledge to conform to the laws, rules and requirements of the Society. Such applications must be endorsed by two Active Members of the Society as

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sponsors, and must be approved by the Board of Trustees. The Board may act by letter ballot upon such application at any time, after which an approved candidate may be enrolled on the proper list of the Society upon payment of the fees and dues prescribed in Section 3.

Contributing Members shall be nominated by an Active Member, and approved by the Board of Trustees, and may be enrolled on the proper list of the Society at any time upon payment of the dues prescribed in Section 3.

All Honorary Members, Active Members, Associate Members, and Contributing Members shall be equally entitled to the privileges of membership, except that only Active Members shall be entitled to vote and hold office. The roster of each grade of membership shall be printed separately, in at least one publication issued by the Society annually. Any person may be expelled from any grade of the membership of the Society if charges signed by five or more active members are filed against him, and a majority of the Board of Trustees examines into said charges and sustains them. Such person, however, shall first be notified of the charges against him, and be given a reasonable time to appear before the Board of Trustees, or present a written defense, before final action is taken by the Board of Trustees.

III.

DUES.

Honorary Members shall be exempt from all fees or dues.

The initiation fee of Active Members shall be ten dollars, and if not paid within three months after the date of their election, the latter shall be null and void. The annual dues for Active Members shall be fixed by the Board of Trustees, and shall not exceed ten dollars.

The initiation fee of Associate Members shall be five dollars, and their annual dues shall be fixed by the Board of Trustees, but shall not exceed five dollars. The privileges of Associate Membership after election shall begin upon payment of the initiation fees, and dues for the first year.

Contributing Members shall pay no initiation fee into the Society. Their annual dues shall be fixed by the Board of Trustees, but shall not exceed twenty-five dollars. The privileges of membership shall begin upon payment of the annual dues.

Any Active Member or Associate Member in arrears for over one year may be suspended from membership by the Board of Trustees, until such arrears are paid, and in event of continued dereliction, may be dropped from the rolls. Active Members in arrears are not eligible to vote. The annual dues of Active and Associate Members are payable within three months succeeding date of annual meeting.

IV.

OFFICERS.

The affairs of the Society shall be managed by a Board of Trustees, consisting of a President, Vice-President, Secretary, Treasurer, and three

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Trustees, who shall be elected from the Active Members at the annual meeting, and hold office until their successors are elected and installed.

The President, Vice-President, Secretary and Treasurer shall be elected for one year, and the Trustees for three years; and no President, Vice-President, or Trustee shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually pertain to their offices, or may be delegated to them by the Board of Trustees or the Society; and the Board of Trustees may, at its discretion, require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Board of Trustees, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officer to execute his duties within a reasonable time, the Board of Trustees, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum, but the Board of Trustees shall be permitted to carry on such business as it may desire by letter.

V.

ELECTIONS.

At the annual meeting, a Nominating Committee of five Active Members, not officers of the Society, shall be appointed, and this committee shall send the names of the nominees to the Secretary at least sixty days before the annual meeting who shall immediately forward the same to the Active Members. Any other five Active Members may act as a self-constituted Nominating Committee, and also present the names of any nominees to the Secretary, provided it is done at least thirty days before the annual meeting. The names of all nominees, provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or self-constituted Nominating Committee, and shall be mailed to every member, not in arrears, at least twenty days before the annual meeting. The ballot shall be enclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary. The blank envelopes shall be opened by three scrutineers appointed by the President, who will report the result of the election at the last session of the annual meeting. A plurality of votes cast shall elect.

VI.

MEETINGS.

The annual meeting shall take place on the first Monday in February, or as soon thereafter as can be conveniently arranged, at such place as the Board of Trustees may decide, at which time a report shall be made by the Board of Trustees, Treasurer and scrutineers of election, and the accounts of the Treasurer shall be audited by a committee of three, appointed by the

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President. Ten Active Members shall constitute a quorum at any regular meeting, and a majority shall rule unless otherwise specified.

The order of business at the annual meeting shall be:

1. President's address.
2. Reading of minutes of last meeting.
3. Reports of the Board of Trustees and Treasurer.
4. Appointment of committees.
5. Old business.
6. New business.
7. Reading of papers.
8. Announcement of election of officers, Honorary and Active Members.
9. Installation of officers and new members.
10. Adjournment.

Other meetings may be held at such time and places during the year as the Board of Trustees may decide, but at least twenty days' notice shall be given of any meeting.

The President shall appoint at the annual meeting a committee of five, to be known as the Summer Meeting Committee, whose duty it shall be to arrange for a summer excursion meeting at some suitable point. The expenses of the Summer Meeting Committee in arranging the program of visits, and for printing, rooms and facilities for meetings, shall be borne by the Society.

VII.

PUBLICATIONS.

The Board of Trustees shall employ, at suitable compensation, an Active Member of the Society as Editor of its publications. The Editor, together with the Secretary and Treasurer, shall constitute a Publication Committee. The Publication Committee shall provide for the publication of an annual volume entitled "Transactions of the American Ceramic Society." This volume shall contain a list of the officers, a list of the members of the Society, classified into grades, a list of the ex-Presidents, the dates and location of meetings, the annual report of the Board of Trustees and Treasurer, the list of prices of the publications of the Society, the rules of the Society, and any other matter pertaining to the business administration of the Society that the Publication Committee may think proper. It shall also contain such of the papers and discussions thereon as the Publication Committee may consider desirable, and each volume shall contain a list of the papers and discussions and an index. The volume shall be six inches wide by nine inches long, and part of the issue shall be bound in paper covers and part in cloth binding. The quality of the paper, the kind of type, the illustrations, and all other mechanical details of the printing and publishing of the books or reprints shall be in the hands of the Publication Committee, subject to the control of the Board of Trustees.

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The acts and policies of the Publication Committee shall at all times be subject to the examination and approval of the Board of Trustees, but the Board shall be bound by contracts entered into by the Publication Committee in the name of the Society. The Publication Committee shall have full power and authority to decide what papers and discussions to publish, which discussions shall be germane to the subject matter, and in what order they shall be published, and in what manner and to what extent they shall be illustrated. In event that the Board of Trustees shall undertake the publication of some other matter or book than the Transactions, the Publication Committee shall act in the same capacity for that publication as in the publication of the annual volume of the Transactions.

One copy of the paper-bound edition of the Transactions shall be sent prepaid to each member of the Society not in arrears. Members desiring cloth-bound copies will be furnished them in place of the paper-bound copy at an increased cost for the binding. No member shall be furnished more than one copy of the Transactions free for any single year. Members cannot purchase extra copies of the Transactions at less than the current commercial rates. A member shall be permitted to purchase one complete file of the publications of the Society at less than the current commercial rate, the amount to be fixed by the Publication Committee and called the Members' rate.

The Secretary shall have the custody of all publications of the Society, shall keep them safely stored and insured, and shall sell these volumes to the public at prices which shall be fixed by the Publication Committee for each new volume as issued. The Publication Committee shall also, from time to time, fix the price of the old volumes remaining unsold, and shall have authority to refuse to sell the old volumes of the Transactions except in sets, at such time as the quantity remaining of any number becomes so small, as in their judgment to warrant such action.

The Editor shall request the author of each article appearing in the Transactions of the Society to fill out and sign, within a definite time limit, a blank form, specifying the number of reprints of said article, if any, which he desires. This form shall contain a table from which can be computed the approximate cost at which any reprints will be furnished. In event that the expense of furnishing the desired number of reprints is large, the Publication Committee may require the author to pay in advance for part or all of the cost involved before the publication of the reprints is begun. On receipt of such signed order within the time limit set, the Editor shall cause to have printed the desired number of copies. If the author makes no reply, or replies after the time limit has expired, then the Society will not be responsible for the publication of any reprints of the article in question, except at the usual market price for the printing of new matter.

No one shall have the right to demand the publication of an article independent of the discussion which accompanied it, and no one having taken part in a discussion upon an article shall be entitled to order reprints of the discussion separately and apart from the article itself.

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The Society is not, as a body, responsible for the statements of facts or opinions expressed by individuals in its publications.

VIII.

PARLIAMENTARY STANDARD.

Roberts "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

IX.

AMENDMENTS.

To amend these rules, the amendment must be presented, in writing, at the annual meeting of the Society, and must be printed on the ballot for officers and sent out not less than twenty days in advance of the next annual meeting, and if the said letter ballot shows an affirmative vote of not less than two-thirds of the total vote cast, then the same shall be declared carried.

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PUBLICATIONS.

The following is a list of the volumes published by the Society and the prices at which they are for sale to the general public:

Description of volume.			Bound in paper.	Bound in cloth.
Vol. I.	1899,	110 pages	$ 4 00	$ 4 75
Vol. II.	1900,	278 pages	4 00	4 75
Vol. III.	1901,	238 pages	4 00	4 75
Vol. IV.	1902,	300 pages	4 00	4 75
Vol. V.	1903,	420 pages	5 00	5 75
Vol. VI.	1904,	278 pages	4 00	4 75
Vol. VII.	1905,	454 pages	4 00	4 75
Vol. VIII.	1906,	411 pages	4 00	4 75
Vol. IX.	1907,	808 pages	5 00	5 75
Vol. X.	1908,	582 pages	5 00	5 75
Vol. XI.	1909,	632 pages	5 50	6 25
Vol. XII.	1910,	882 pages	5 50	6 25
Vol. XIII.	1911,	837 pages	5 50	6 25
Vol. XIV.	1912,	— pages	5 50	6 25
Complete set			$65 00	$75 50

The Board of Trustees established in the beginning a differential between members of the Society and others, in the matter of prices to be paid for copies of the Proceedings. This differential has been changed from time to time as volumes have grown scarcer and sales increased. The present arrangement, which will stand until March 1, 1913, allows a straight discount of 40 per cent. to members in good standing. Members in arrears are not furnished copies of the volume for the current year, nor allowed the discount for the older publications. Members are also not permitted to purchase more than one full set of the publications at members' rates. The care and sale of the Publications has been transferred to the Publication Committee, which reserves the right to change the discount from time to time on any one volume or on all, as may be necessary.

The number of copies of the earlier volumes is not large, and members are advised to procure full sets as soon as possible. The prices will never be less and will certainly raise as time goes on.

In addition to the above volumes of the Transactions, the Society has also published the following books, which will be sold *net* at the prices listed to the public and members alike:

The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (*a*) Treatises of a General Scientific Nature. (*b*) Essays Relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages, 552. Bound in cloth ..... $ 7 50

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The Collected Writings of Dr. Hermann August Seger, Volume II. (*b*) Essays on White Ware and Porcelain. (*c*) Travels, Letters and Polemics. (*d*) Uncompleted Works and Extracts from the Archives of the Royal Porcelain Factory. Pages, 605. Bound in cloth..... $ 7 50

A Bibliography of Clays and the Ceramic Arts, by Dr. John C. Branner, 1906, 451 pages. Bound in cloth. Contains 6027 titles of works on Ceramic subjects..... $ 2 00

The above publications will be shipped at the consignee's expense, by express, to any address on receipt of the price. All checks or money orders should be made payable to The American Ceramic Society, and not to the Secretary or the Treasurer.

EDWARD ORTON, JR.,
Secretary.

Columbus, Ohio.

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ANNUAL REPORT OF THE BOARD OF TRUSTEES.

COLUMBUS, OHIO, March 1, 1912.

To the Members of the American Ceramic Society:

The Board of Trustees submit herewith their report of the affairs and condition of the Society for the period February 1, 1911 to March 1, 1912. The period has been lengthened to thirteen months in this case, because of the date finally set by the National Clay Products Exposition Company for their enterprise. Incidentally, this change in date has been found to be of very great advantage to many of the members, for whom the first week of February is about the worst time possible, on account of the mid-year examinations and registration at the Universities, and it seems that the change might well be made permanent.

VOLUME THIRTEEN.

The most important concrete thing which results from the existence of our organization is the library of useful technical literature which it has produced. If the Society were blotted out of existence to-day, its publications would assure it a permanent and honored place in the history of the ceramic art. In these thirteen years it has published 384 papers, aggregating 5,382 pages of actual technical matter, not including the business section in the front of each volume and the indices which have been prepared for the last four volumes.

Of this amount, 53 papers were contributed last year, the largest number of any year in our history, corresponding to a growth of 20 per cent. These papers cover 770 pages, an amount exceeded by but one year's record. In fact this increase in number of papers, with a decrease in volume, is to be construed as a distinct gain, and a tribute to the energy and patience of our editor, Mr. R. C. Purdy, whose efforts to condense the volume have confronted him with the difficult and ungracious task of cutting out the unnecessary and trivial, and retaining the real essence of what is brought before the Society. How well he has succeeded is known to all who have studied the volume.

As to the mechanical side, the book has been printed by an eastern firm, of large experience in similar work, and with a distinct gain in efficiency and quality in the result.

There has been some increase in cost, but in the opinion of the Publication Committee, the results justify the increase.

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FINANCIAL CONDITION.

The financial condition of the Society is shown in the following statement:

Income

Brought forward from preceding year		$ 151.84
Receipts from dues:		
63 Active members (1911–'12) @ $5.00	$ 315.00	
1 Active member (prepaid for 1912–'13)	5.00	
334 Associate members (1911–'12) @ $4.00	1,336.00	
12 Associate members, covering various arrears	38.71	
13 Associate members, covering various advance payments	58.70	
1 Contributing member (1912–'13), paid in advance	25.00	
Receipts from initiation fees:		
8 Active members @ $5.00	40.00	
63 Associate members (1911–'12) @ $5.00	315.00	
5 Associate members (1912–'13) @ $5.00 paid in advance	25.00	2,158.41
Receipts from sale of publications:		
211 Volumes Transactions	867.63	
10 Volumes Branner Bibliography	14.74	
16 Volumes Seger's Collected Writings @ $7.50	120.00	1,002.37
Extra for cloth bindings	143.78	143.78
Receipts from authors for reprints	129.89	129.89
Receipts, miscellaneous	3.33	3.33
Total received		$3,589.62

Disbursements

Cost of publication of Volume XIII:		
Stenographic report	$ 135.85	
Illustrations, drawings and engravings	332.29	
Printing, binding and casing	1,578.55	
Editor's salary	600.00	2,646.69
Paid for 15 volumes Seger's Collected Writings	68.74	
Paid for authors' reprints	129.89	198.63
Paid for Secretary's office:		
Salary, assistant secretary (13 months)	325.00	
Postage, stationery and supplies	123.15	
Telegrams	4.25	

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Expressage on books prepaid	72.54	
Index cabinet	3.60	
Insurance and interest	29.18	
Binding early volumes of Transactions	38.50	
Expenses for 13th convention	50.26	646.48
Total		3,491.80
Balance in bank		97.82
Grand total		$3,589.62

Outstanding Assets

Dues and fees	53.26	
Sale of publications	95.01	148.27

Outstanding Liabilities

None

A study of the foregoing shows the following facts:

First.—There has been a shrinkage in actual new revenue collected this year, as compared with 1910–'11, amounting to about $161.76. To pay our bills and take care of the business, we have been obliged to use all available funds, so that we have to carry forward to the new year a smaller balance than before, *viz.*, $97.82. On the other hand, we have assets in the form of uncollected accounts to the amount of $148.27 of which the larger part is good, so that the Society is in a sound condition, without considering the capital tied up in the form of unsold publications.

Second.—There has been a decrease in the sales of our publications this year, amounting to $244.82.

Third.—There has been a gratifying increase in the receipts from membership dues and fees, almost exactly compensating for the loss in item 2, *viz.*, $259.56.

Fourth.—The cost per volume of Volume XIII has decreased a few cents per copy, but the gross cost of the edition has increased by $269.46. This is due partly to a higher rate for the printing, but also largely to the fact that we had 100 more books printed to take care of our growing membership list and expected increase in sales.

Fifth.—On October 23, 1911, in order to handle the financial situation promptly and satisfactorily, the Board of Trustees borrowed $650.00 at the bank when Volume XIII was delivered, and paid off the printer promptly. They took up the debt as the money came in, discharging it completely in February, 1912. The interest cost of this procedure was $9.18.

Sixth.—This would not have been necessary if the members would make a change in their ways, by paying their dues promptly. No one except the

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officers concerned has any conception of the waste of time and energy required to collect the dues from members who are entirely able to pay, and who always do pay in the end.

Seventh.—The Society should find without further delay, some effective means of increasing its revenue by several hundred dollars per annum. Its present solvent condition is maintained only at unreasonable expenditure of energy.

DUES.

The rules were amended a year ago to make possible an increase in dues. The policy involved in this change has been carefully considered by your Board. On the one hand, it is obviously wise to keep the dues and fees as low as possible, consistent with a good progressive administration of the Society's business. Increase of the dues may fail of its object, which is increasing the revenue, by causing a shrinkage in our present roster, and by making new members more difficult to secure. On the other hand, it is apparent from the financial statement, that the work of the Society is being handled with no financial margin, and that by only very hard work is it possible each year to avoid a deficit.

It seems to the Board that in such an organization as ours, the receipts from dues and fees ought to be sufficient to cover the actual cost of publishing a reasonable supply of the current volume of Transactions, leaving the ordinary expenses of administration to be borne by the sale of the back numbers. Reference to the foregoing statement shows:

Cost of publishing Volume XIII	$2,646.69
Receipts from dues and fees of members including extra payment for cloth bindings	2,302.19
Deficiency	344.50
Cost of administering Society's business (excluding reprints, which exactly pay for themselves)	715.22
Realized from sale of literature, other than that covered by dues	1,002.37
Surplus	287.15

Allowing for the reduction in cost, if only the required number of copies to go around were printed, the above figures show that the members are getting their volumes at less than cost, and are therefore profiting at present from the work done in previous years by themselves or others. The Board thinks that the sentiment of the members will support such an increase in dues as will clearly cover the cost of publication, and announces the following rates for the current year:

Active members	Initiation fees	$10.00
	Dues	7.50
Associate members	Initiation fees	5.00
	Dues	5.00

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The income at these rates should pay the Society's expenses, unless a falling off in membership should result from the change.

PUBLICATIONS.

The stock of the publications of the Society, which constitutes its sole capital in the financial sense, has been compiled from the books as follows:

Number of the volume	Number remaining on hand Feb. 1, 1911	Received since	Disposed of by sale	Disposed of otherwise	In stock March 1, 1912, by book account
I	190	...	12	..	178
II	166	...	15	..	151
III	188	...	12	..	176
IV	159	...	11	..	148
V	128	...	12	..	116
VI	158	...	14	..	144
VII	156	...	11	..	145
VIII	149	...	13	..	136
IX	113	...	13	..	100
X	144	...	16	..	128
XI	165	...	16	..	149
XII	167	...	32	..	135
XIII	...	700	434	22	244
Branner bibliography	825	...	10	2	813
Totals	2,708	700	621	24	2,763

The sale of the Transactions has been greatly simplified this year by the adoption of a fixed price list, from which two discounts are allowed, *viz.*, 20 per cent. for libraries and book-dealers, and 40 per cent. to members desiring to obtain complete sets. This system has worked well, and will be continued. Regarding the matter of increasing prices on volumes which are becoming scarce, the Committee has fixed a definite limit of 100, below which copies will not be sold except as part of an order for a complete set, or to fill a gap in a partial set previously purchased. Volume IX is thus already withdrawn from unrestricted sale, and Volume V will soon reach this point.

The value of the Society's property is difficult to determine. If sold slowly, as thus far, it will realize a mean price of about $3.70 per volume for the Transactions. The bibliography is of little value, not more than $100.00 and probably less. On this basis, the property is worth about $7,325.00. If sold in a lump, of course no such figures could be obtained.

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ROSTER.

The roster of the Society still continues to grow nicely. The figures are as follows:

Brought forward February 1, 1911:		
Honorary members	2	
Active members, resident	51	
Active members, foreign	3	
Associate members, resident	292	
Associate members, foreign	33	
Total	381	
Accessions during the year 1911–'12:		
By election to active membership, resident		10
By election to active membership, foreign		1
By election to associate membership, resident		67
By election to associate membership, foreign		3
Total		81
Losses during the year 1911–'12:		
By death, active members, resident		2
By death, active members, foreign		0
By death, associate members, resident		0
By death, associate members, foreign		1
By resignation, active members, resident		0
By resignation, active members, foreign		0
By resignation, associate members, resident		21
By resignation, associate members, foreign		0
By promotion in grade, associate members, resident		10
By promotion in grade, associate members, foreign		1
By transfer from resident to foreign associates		2
Total		37
Status, March 1, 1911:		
Honorary members	2	
Active members, resident	59	63
Active members, foreign	4	
Associate members, resident	327	360
Associate members, foreign	33	
Total		425

The gain in active membership is 10 (18 per cent.); associate membership is 36 (11 per cent.); the mean gain is 46 (12.6 per cent.).

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SUMMER MEETING.

For the first time in several years no summer meeting was held in 1911. The principal cause for this failure was the fact that no committee on arrangements was appointed at the Trenton meeting, as had been done at several preceding meetings, to look after the summer meeting and arrange a schedule. The Secretary's engagements did not permit him to take the work on alone, and after some little correspondence and effort to get a voluntary committee to serve during the summer without success, the matter was abandoned. The policy of retaining a summer meeting has been before the Society on numerous occasions, and while it has uniformly been agreed that such a meeting is useful, the fact remains that it has been difficult to keep the custom alive.

During the summer of 1912, two international associations visit this country, the Eighth International Congress of Applied Chemistry, and the International Society for Testing Materials. Both of these organizations meet, one in New York and the other in Washington, in the early part of September. In both of them, foreign ceramists will be present. Already the German Society for Clay, Cement and Lime has asked coöperation from us in the matter of arranging an itinerary among ceramic plants. The opportunity for the American Ceramic Society to step in and facilitate the purpose of our foreign brothers is thus at hand, and it could be managed so that we should either accompany them on their itinerary, or we should meet them at a certain place and give them a welcome there. This whole question should be taken up and discussed by the Society.

CONTRIBUTING MEMBERSHIP.

The contributing membership plan has been slow in coming into operation. But at last we have overcome all difficulties in the rules and have made a start. One such member has voluntarily come forward for the year 1912–'13. Doubtless others can easily be secured. If secured at all this year, it should be in time for publishing the list in the annual volume.

CONCLUSION.

In conclusion, the Board of Trustees congratulates the Society upon the successful year's work. We have published an excellent volume, have paid our bills, owe no money, and have a good program arranged for our fourteenth meeting, and meet with prospects bright for another successful year.

For the Board of Trustees,

EDWARD ORTON, JR.,
Secretary.

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IN MEMORIAM.

EDWARD R. TAYLOR.

Edward R. Taylor came of a family of potters and in his early years worked for his father, who was a manufacturer of earthenware. He was born in the year 1838 at Hanley, Staffordshire, England, and after a brief experience in the factory he entered the local art school. His success was such that he secured a scholarship at the South Kensington School and was afterwards appointed, when only twenty-four years of age, principal of the school of art at Lincoln.

From this time, Mr. Taylor's success was assured. He won fame as an artist as well as a teacher and numbered among his friends some of the best known painters of the day. He was appointed to the Birmingham School of Art in 1878 and remained in charge until his retirement in 1903. He then, though sixty-five years of age, determined to devote himself, in conjunction with his son, W. Howson Taylor, to the production of fine decorative ceramics. Together they founded the Ruskin Pottery, and the beauty and originality of their wares have attracted the notice of critics and connoiseurs on both sides of the Atlantic. At the World's Fair at St. Louis in 1904, the Ruskin Pottery was awarded the Grand Prix. Mr. Taylor died on Januray 14, 1912, in the seventy-fourth year of his age.

SAMUEL VERNON PEPPEL.

Samuel Vernon Peppel was born at Leetonia, Ohio, September 30, 1870, where he spent his boyhood and youth. He entered the Ohio State University in 1896, and took the degree of B.Sc. (in chemistry) in 1899. He elected as much ceramics as was possible in his course for the above degree and became identified with the ceramic field at once on graduation.

His first work upon leaving the university was as chemist to the Wisconsin Geological Survey, under Dr. E. R. Buckley. He remained here about one year, and his labors formed the basis of the chemical section of the report upon the clays of that state.

Leaving Wisconsin, he was employed on the Geological Survey of Ohio in 1901–'03, collecting data on the limestones and the lime industry of the state, and also in an experimental study of the sand-lime brick industry. His studies here resulted in several chapters on lime manufacture and testing, in *Bulletin* 4, and a complete treatise on the sand-lime brick industry, composing *Bulletin* 5, publications of the Geological Survey of Ohio. Mr. Peppel's work in both lime and sand-lime brick was pioneer work in this field in America and has not been surpassed at this date.

He next took a position on the technical staff of the journal, "Rock Products," dealing chiefly with the clays, limes, cements, and mortar materials. This experience was not to his taste, as he was essentially a student

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and research man and not a journalist. He resigned this work in about a year and established a chemical laboratory in Columbus, Ohio, in 1906 for the clay, lime and cement industry. He maintained this laboratory successfully for three years, and did some occasional research work for publication. In 1909, he sold out his laboratory, and went to Chicago as chemist for the United States Gypsum Co., continuing there until he died.

Mr. Peppel was a man of small stature, and wiry build, with keen incisive features and reserved manner. This reserve made it difficult for him to know others or let others know him, and hence he was never widely appreciated at his true worth. In the small circle of those who really knew him, he was much loved, for no more unselfish or kind man ever lived. He would go to any length to oblige a friend, even to his own detriment. His health was never rugged, and the laboratory work which he loved was not conducive to maintaining his vigor. He allowed himself frequently to overwork until a fit of sickness compelled a halt, and in such an attack, he passed away on August 21, 1911, at Chicago. He was married in 1909 to Miss Josephine Chandler, whom he leaves to mourn him. The American Ceramic Society has lost a firm supporter by his premature death.

MARK OGAN.

Mark Ogan was born at Nelsonville, Ohio, October 12, 1874, and lived for some years in that and near-by towns. That he early manifested a strong bent for practical and scientific matters is shown by the fact that he had become engineer and electrician for the electric light plant at McArthur, Ohio, some years before he decided to secure a technical education.

He entered the Ohio State University in 1901, electing the short course in clayworking. Although unused to school methods, he rapidly became one of the best pupils in his class. He was intensely in earnest and left nothing undone which would help him to his goal. Rarely is a student found who so fully realizes the importance of thoroughness.

Leaving school in 1903, he first went with the Atlantic Terra Cotta Co. at Rocky Hill, N. J. In a little time, he overcame completely the suspicion and distrust which practical men generally manifest toward a green collegian. He had been a practical man himself before he was a student and knew how to win the confidence and friendship of men. He stayed here a year or more, working in all departments, and gaining the experience he coveted. He then resigned to take a foreman's position in the M. E. Gregory Terra Cotta Co. at Corning, N. Y. From here, he went in six months to St. Louis, to take a position as chemist and estimator for the St. Louis Terra Cotta Co. Thus, in three short years, he had passed through every part of the terra cotta business and become competent to take any duty in connection with this complicated industry.

He remained at St. Louis several years, resigning to take a better place at Tesla, Calif., as manager of the terra cotta department of the Carnegie Brick & Pottery Co. His last position was as chemist and superintendent

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MARK OGAN.

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of the Northern Clay Products Co. at Auburn, Wash., where he was most successful in producing excellent terra cotta from somewhat variable and difficult materials.

Mark Ogan was a singularly winning and lovable man. Although a citizen of Auburn for less than a year, the death was mourned by the whole community, so fully had he won the confidence and affection of all. His power lay in his personal knowledge of the workman's side of life, and his kind and sympathetic attitude to all who labor. At the same time, his dignity and poise prevented any from imposing upon these lovable human traits, so that he was efficient as a superintendent.

His life emphasizes the tremendous influence which persistent adherence to an ideal will exert. He selected the terra cotta industry as his goal while at school, and although beginning his education late and with a poor foundation, he made himself one of the most competent and efficient men in his line in the country. He would sacrifice the present good for the final gain, as few young men could.

His interesting career was cut short by an attack of appendicitis, which was not properly diagnosed or treated until too late. He died May 11th in a hospital at Seattle, Wash., after making a most gallant fight for his life. His thoughts dwelt repeatedly during his last illness upon the American Ceramic Society, in which he was profoundly interested, and of which he was proud. The Society joins with his widow and parents in mourning the loss of a capable ceramist and a true man.

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PAPERS AND DISCUSSIONS.

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THE AMERICAN CERAMIC SOCIETY.

ADDRESS OF THE RETIRING PRESIDENT.

To-day the American Ceramic Society celebrates its fourteenth annual gathering.

When we look back over the path up which we have journeyed, accompanied as we were with doubt and uncertainty, and view the commanding position we have now attained, we feel coming over us a sense of confident composure; a sense of pleasant security; a sense of work well done, which time nor all that is at enmity with human worth and progress can ever mar or destroy.

The present cannot forget the past, for upon it all our joys, all our hopes, all our accomplishments are founded; in it are treasured not only all that we are, the work we have done, but the means by which its value may be measured. That we may better appreciate and understand our past, therefore, let us look backward for a moment and view again the spot where we once stood.

In the year 1898, in Pittsburgh, sat three gentlemen engaged in earnest conversation, exchanging thoughts upon the subject of ceramics: its present condition, its future prospects, and the means to be employed in looking toward its advancement. Little or no literature on the subject was to be found except that written in a foreign language. Science as applied practically to ceramics was but little known. No organized effort had ever been put forth to gather together existing knowledge or to establish a foundation for further research and enlightenment Whether or not, in the light of the indifference then existing, such an effort could be made successfully was a problem. Many of those interested commercially in ceramics had little faith in science and less desire to adopt it. Theirs was the one industry in which science had no part.

These men, however little the interest manifested by those from whom they might have expected support, decided to enlist the interest of their ceramic friends with a view of seriously considering the matter of organization. The proposition was well received, and so much enthusiasm was aroused that in the

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following year (1899), at Columbus, Ohio, the birth of the American Ceramic Society was formally announced, and its aim—advancement of scientific ceramics—was published.

This creditable undertaking, like all ambitious awakenings, was born among difficulties. To prosper, it needed strong men, men with earnest purpose, men with zeal, men with that ability and determination which never entertains defeat.

To better appreciate and understand the characteristic *spirit* of the organizers of this Society, it is only necessary to recall a letter which the speaker received some years ago from our Secretary calling upon him to write a paper. In this, the Secretary urged him not to give the usual excuse, "Too busy," but to remember that it was to the busy man alone that the world was indebted for its progress and welfare, and to the busy man alone the Society looked for its support. This, then, was the spirit that took hold of our Society in its infancy, and as we hastily review its history and the quality of its work, we shall see that like the path star to the lone traveler, it never failed to make the treading sure.

No sooner was the Society organized than it took upon itself the laborious and expensive task of translating into English the masterful work of a German whose name has become as familiar in ceramics as Raphael's in art. Seger was one of the pioneers in scientific ce amics, and so valuable was his work considered, fragmentary as it was, that the Society, then consisting of so few members, decided to take up the task of its translation. It was an expensive operation and the youthful Society was without funds, yet benefitting by the work already done by Prof. Orton and others, the task was taken up and, after the expiration of four years, was successfully completed. Its publication was a credit to the Society and an honor to all who assisted in the work.

In the meantime, our Society was increasing in numbers; our publications were enlarging both in size and in quality. Not only was interest increasing at home, but the Society was attracting attention abroad. Nature's secrets, though once enveloped in mystery, were under intelligent and uncompromising effort being made clear to man's understanding. The mountains

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of difficulty and doubt were thus melting away in the sunlight of knowledge and truth, for science not only develops the facts themselves but it expands the perceptive qualities of the mind, making comprehension and intelligent application of these facts possible.

Valuable effort is not always immediately recognized, but recognition of such effort is oftentimes an indication of its worth. Imitation is the profoundest compliment any work can receive. To be recognized, to be imitated, to see our work taken up by others, and by them passed on to further usefulness and influence, is, therefore, an indisputable evidence of its worth.

Since the establishment and success of the American Ceramic Society—the first of its kind in the country—there have been as a result of its influence other similar societies organized in Europe. It has also been the means of organizing ceramic classes in several towns; and in some cities (like the city of Trenton) there have been ceramic schools established and beautiful buildings erected for the study and advancement of scientific ceramics.

Its publications have grown, its influence has enlarged far beyond the hopes of its founders. Its first volume of one hundred and ten pages consisted of eight papers and five separate discussions of announced subjects. Our next and succeeding volumes contained a large and ever-growing number of papers all of which show remarkable progress while some are characterized by deepest thought, attacking difficult problems with a clearness and power never before evidenced in ceramics. To-day, our latest volume contains eight hundred and thirty-seven pages and treats exhaustively of forty-five different subjects. Taken together, the published works of our Society probably exceed in volume and variety of subjects the total of all other publications upon the subject of ceramics in the English language Thus, both in extent and in value, our ceramic literature has passed from poverty to great riches, affording the student of to-day a field for labor golden with profit.

It may be interesting to note here that of the eight gentlemen who presented papers at out first meeting, six are still members and two have papers at this meeting. Of the twenty-three who took part in the discussion in our first meeting thirteen years

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ago, seventeen are still members and four have papers at this meeting.

It has been wisely said that every age has its problems by solving which humanity is helped forward (Heine). Thus it is to the wrinkled brow of thought the world is indebted for its progress. To think is to develop; to think is to labor; and when that labor is productive of worthy results, they should be recorded, not as a monument to our own efforts, but as an inspiration to further and more enlightened effort on the part of those who follow. Humanity of all ages pays dutiful homage to the thinkers who have emancipated them from the bondage of darkness and doubt.

Thus it is we bow to the Lafevers, the Bourrys, and the Segers, in scientific and to the Mintons, the Coultons, the Wedgewoods, in practical ceramics; for it is to those who toiled when the light was low and the promise small that we owe so much. They were to ceramics what Schopenhaur was to philosophy; what Adam Smith was to political science; what Hipparchus was to astronomy. They opened up a new line of thought and action, out of which sprung the foundation of our present knowledge. This was the inheritance time bequeathed to us. To enrich it with the jewels of advanced thought is our obligation. To this duty the American Ceramic Society committed itself fourteen years ago. Is it not accomplishing the task?

We have thus far spoken only of the educational influence of the Society. What can we say of its value practically?

Fourteen years ago, there was little to encourage the student of scientific ceramics. The feeling among ceramic manufacturers generally was unfavorable to the students or "paper potters," as they were termed. Fancy theories could not take the place of practice, for practice was the real work while science appealed only to the imagination. They were in business for profit and had no interest in the visionary baubles of the scientists. They were satisfied with the old slow methods of locomotion, and it was with deep satisfaction that they pointed to the occasional wreck of a "high flyer." We are willing to grant that in the light of some of the bungles made in the name of science, their opinions were excusable; yet there was a flaw in their judgment for they

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were condemning the principle while the fault lay only with the man.

The founders of this Society were familiar with this deep rooted prejudice and fully realized the difficulty of their task. They knew that to triumph in this, as in other departments of human endeavor, exacted a spirit of sacrifice. They were seeking to give a new direction to ceramic thought and practice, and, like in all past efforts for intellectual advancement, the old school thundered against the new But, as in the past, the progressive forces became invincible; time has weighed the issue, and, thanks to the intelligence of the opposition, the new values are becoming universally accepted The scientific and the practical man, about whom there has been so much discussion, are fast becoming one both in spirit and in practice.

In this our Society has met with signal triumph; yet not alone has it distinguished itself in this test of practical worth; not alone has it opened up the ceramic world to the students of scientific ceramics, creating a want, Prof. Orton tells us, which the graduates of all the schools cannot supply; not alone has it brought the manufacturer into harmony with its efforts; but it has in a large measure brought about a more liberal spirit among the manufacturers themselves. This is in line with modern wisdom, for it has been our opportunity to witness several total failures in business due to this spirit of "close communion." We may flatter ourselves with the thought that we have fathomed the deepest depths and climbed the greatest heights; but suddenly there comes a flood which at first we refuse to notice, but which finally overwhelms us, whereas had we observed the policy of "open arms" we might with our successful neighbor have been carried along with the tide that is ever sweeping successfully onward.

We are acquainted with some of the manufacturers' difficulties in reaching this new standard in ceramic ethics, for we are acquainted with some of their griefs.

The scientific man evolves a new law, he marvels at its possibilities; yet its value only reaches its height when he takes the world into his confidence. The world's approval is his compensation. Not always is it so with the manufacturer nor with his

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assistant known as the "practical man," for here silence seems more profitable. His value is weighed in the commercial scale and is heavier or lighter as his knowledge is greater than his neighbors'.

We have heard it said that there is not one law in ceramics that can be credited to the practical man. If this be true, we offer the above as its explanation—yet we are loath to accept it. We cannot view the works of the old masters, the beauty of their designs, the magnificence of texture, the harmony of color, and the perfectness of their execution—never surpassed if ever equaled in modern times—without attributing to them some knowledge of the laws governing successful production. We are not prepared to accept that even to-day there are any of our most successful, practical men but that have evolved some guiding rule in their practice whose constancy has dignified it into law. All have their methods, and while some are hap-hazard, in others there is something more than madness; and had we intimate knowledge of their work and methods, we might discover some law in their practice even though it has not reached the dignity of being publicly recorded.

But the day of profit in secrecy is past, for the development in ceramics, while sure, is so moderate of pace that the genius "Hard Work" may stumble and still catch up. Progress in ceramics does not move with startling rapidity as it does in some of the newer sciences, for in ceramics the marvel of to-day has been promised so long that its presence has become familiar and we have prepared ourselves to receive it. That the workers in ceramics are fast coming to realize the futility of secrecy is more apparent to-day than ever A more congenial and family spirit has been aroused which cannot fail to result in material benefit, and which is conducive to much more rapid and satisfactory progress.

For these happy conditions brought about by fourteen years of effort on the part of the American Ceramic Society, we extend it our hearty congratulations.

We have endeavored in this short address merely to mention a few of the important accomplishments of our Society; but

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there are many others worthy of a place here but which our privilege in space will not permit us to consider.

We have no startling recommendations for our Society's future consideration. We would like to mention, however, that it might be well to consider the advisability of copyrighting our "Transactions." We have received letters during the year asking for information as to which of the various magazines or periodicals published our "Transactions." The sale of our volumes is one of our biggest assets, and could the information be secured in no other way, it might result in such increased sales as would warrant the expense of copyrighting. There may, however, be more weighty reasons for not doing as suggested.

We have all no doubt noticed with pleasure the energy as well as the enterprise which our Editor has put into his work. His method of insisting upon the members adding written discussions to such papers as they are most familiar with is, in our judgment, a good one. It adds much interest to the work.

And now, fellow-members of the American Ceramic Society, before I vacate the high place to which you unwittingly chose me a year ago, I want to take you into my confidence a moment that I may in a manner befitting my feelings express to you the deep sense of gratitude I feel toward you for the great honor and for your kind help and consideration in my efforts to perform the duties of the office. Its value is not measured by gold. Its compensation is not that which fades with the day, but that which in memory lives on through the years, abiding ever, linking itself with the greatest joys of our life; for of all the glory the earth has to give, none is greater either to the weak or to the strong, than that received through the knowledge that opportunity, even though clothed in sacrifice, enabled us to add our mite to the world's education and progress.

Soliciting on behalf of my successor the same kind treatment you have accorded me, I again thank you, one and all.

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INFLUENCES OF VARIABLE SILICA AND ALUMINA ON PORCELAIN GLAZES OF CONSTANT R O.

By R. T. STULL, Ceramic Laboratories, University of Illinois.

INTRODUCTION.

Porcelain glazes of the Seger cone formula type are the most inexpensive to produce synthetically, have a comparatively wide range of maturing temperature and give but few defects. These are offered as the principal reasons for the comparative meagerness of literature pertaining to investigations on glazes of this type.

Seger[1] gives the following as glaze formula commonly used for porcelain:

$$RO,\ (1 \text{ to } 1.25)\ Al_2O_3,\ (10 \text{ to } 12)\ SiO_2$$

and for Seger porcelain[2]

$$RO,\ 0.5\ Al_2O_3,\ (4 \text{ to } 6)\ SiO_2$$

Prof. Orton[3] gives the following limits for characteristic porcelain glazes:

$$\left.\begin{matrix} 0.1 \text{ to } 0.5\ K_2O \\ 0.9 \text{ to } 0.5\ CaO \end{matrix}\right\} 0.5 \text{ to } 1.25\ Al_2O_3,\ 4.0 \text{ to } 12.5\ SiO_2$$

EXPERIMENTAL WORK.

In a study of porcelain glazes[4] of the cone formula type, two groups were made in order to illustrate the influences of variable silica and alumina. The first group covered the limits

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.7\ CaO \end{matrix}\right\} 0.3 \text{ to } 1.0\ Al_2O_3 \Big\} 1.8 \text{ to } 7.2\ SiO_2$$

and comprised eight horizontal series, from A to H, containing eighty glazes in all.

The glazes in that portion of the field covered by the A to H series were made by blending the four extremes according to their combining weights. The formulae and batch weights of these extremes are:

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[1] Vol. II. Translations Seger, p. 705.
[2] Ibid., p. 706.
[3] Glaze lectures at Ohio State University, 1901–2
[4] Work done by classes 1911 and 1912, University of Illinois.

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Glaze	K_2O	CaO	Al_2O_3	SiO_2	Canadian feldspar	$CaCO_3$	Clay: Eng. c.c. No. 7	Clay: Tenn. b.c. No. 7	$Al_2(OH)_6$	Ohio flint
A–1	0.3	0.7	0.3	1.8	167.1	70.0	..	..	...	...
A–10	0.3	0.7	0.3	7.2	167.1	70.0	..	..	...	324.0
H–1	0.3	0.7	1.0	1.8	167.1	70.0	..	..	109.2	...
H–10	0.3	0.7	1.0	7.2	167.1	70.0	90.3	90.3	...	240.0

Glazes in the W to Z series were also made in the same manner with the exception that it was necessary to employ a frit in order to introduce the excess K_2O which could not be furnished by feldspar. The formulae and batch weights of the four extremes are:

	K_2O	CaO	Al_2O_3	SiO_2	Frit	Feldspar	$CaCO_3$	$Al_2(OH)_6$	Flint
W–02	0.3	0.7	0.25	0.6	85.6	...	50.0	23.4	...
W–6	0.3	0.7	0.25	4.8	21.4	125.3	65.0	...	198.0
Z–02	0.3	0.7	0.10	0.6	85.6	...	50.0	...	...
Z–3	0.3	0.7	0.10	3.0	85.6	...	50.0	...	144.0

Frit for the above:

0.6 K_2O } 0.2 Al_2O_3 1.2 SiO_2
0.4 CaO }
Comb. wt. = 171.2

Feldspar = 111.4
K_2CO_3 = 55.2
$CaCO_3$ = 40.0

Crazing is comparatively rare in this type of porcelain glaze, due to the vitreous nature of the body and the similarity in composition of body and glaze. In order to intensify crazing and to locate that portion of the field in which it would be most likely to occur, the glazes were applied to porous, biscuit wall tile, which shrunk considerably but were still porous at the end of the burn.

The glazes were applied a little thicker than is customary in practice, and the trials set in tile saggers and burned to cone 11 in 36 hours. The results are shown graphically in Charts I and II.

DISCUSSION OF RESULTS.

On Chart 1, the molecular variations of silica are plotted along the abscissa and the molecular variations of alumina along

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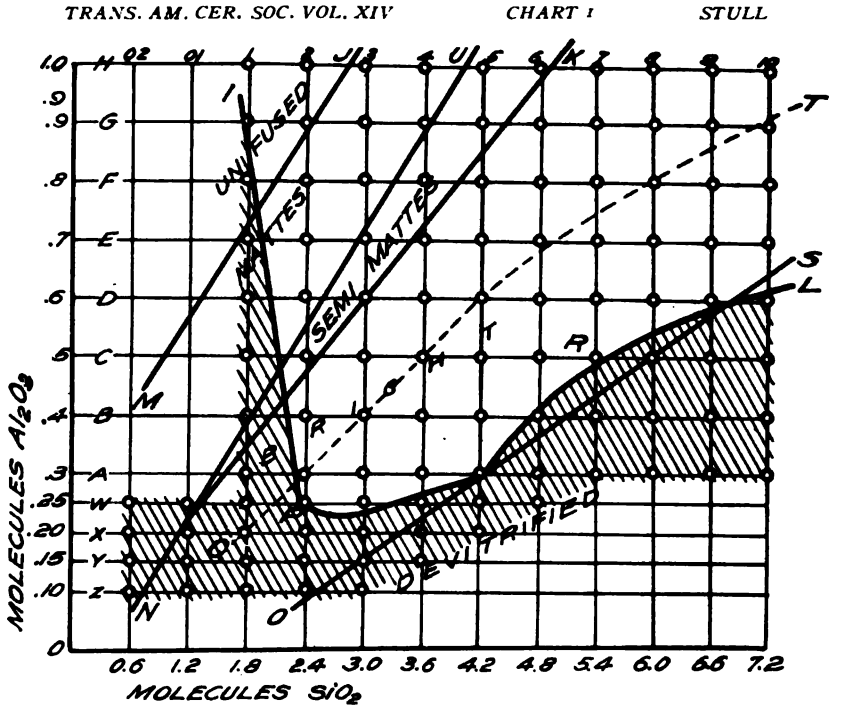
the ordinate. The letters at the left denote the horizontal series



and the numbers along the top the vertical series, so that each glaze is located by a letter and a number.

Since the RO for all glazes is constant, $\left\{\begin{matrix}0.3\ K_2O \\ \\ 0.7\ CaO\end{matrix}\right\}$ the formula of any glaze can be read from the chart by referring to the ordinate for its alumina and to the abscissa for the silica. For example, the formula of E–5 is $\left\{\begin{matrix}0.3\ K_2O \\ \\ 0.7\ CaO\end{matrix}\right\}$ $0.7\ Al_2O_3\ 4.2\ SiO_2$. The alumina is constant in a horizontal series while the silica varies. In a vertical series the silica is constant and the alumina is the variable.

To the left of the line M J are the underfired mattes, and

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between M J and N U are the matured mattes. Between N U and N K are mattes showing a sheen or slight gloss and designated as semi-mattes. The bright glazes occur between N K and O S, and below O S the glazes are devitrified. The glazes are all crazes below the line I P R L and all sound above this line. The dotted line Q T passes through highest gloss of each series.

Beginning at the ordinate on Chart 1 and moving to the right parallel to the abscissa, it is observed that crazing and matte texture decrease with increase in silica, and that brilliancy increases up to the axis of highest gloss, Q T, beyond which brilliancy decreases, crazing increases and finally devitrification occurs.

Moving from the abscissa upward parallel to the ordinate, we see that increasing alumina has decreased crazing of glazes both high and low in silica, has decreased devitrification in high silica glazes, and increased matteness in low silica members.

A comparison of the influences of variable Al_2O_3 with those of variable B_2O_3 is of interest. It has been shown[5] that increasing B_2O_3 decreases devitrification and crazing in high silica glazes and increases crazing and decreases matte texture in low silica glazes. B_2O_3 and Al_2O_3 then function the same in high silica glazes but function oppositely in low silica glazes.

In Chart 2, the glazes are located by the molecular ratios of silica to alumina on the abscissa and by the total oxygen ratios on the ordinate. The molecular ratio of silica to alumina is independent of the total oxygen ratio, but the total oxygen ratio is partly dependent upon the silica-alumina ratio. Therefore, in plotting glaze groups similar to Chart 2, the evidence presented is influenced by one dependent and one independent variable. This must be borne in mind in drawing conclusions, otherwise they may be misleading.

The underfired mattes occur at 1, crazed mattes at 2, sound mattes at 3, semi-mattes at 4, crazed brights at 5, sound brights at 6, and glazes which are crazed and devitrified at 7. The line A B is the high gloss axis.

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[5] "Opalescence and the Function of B_2O_3 in the Glaze," Trans. A. C. S., Vol. 12, pp. 119 to 137.

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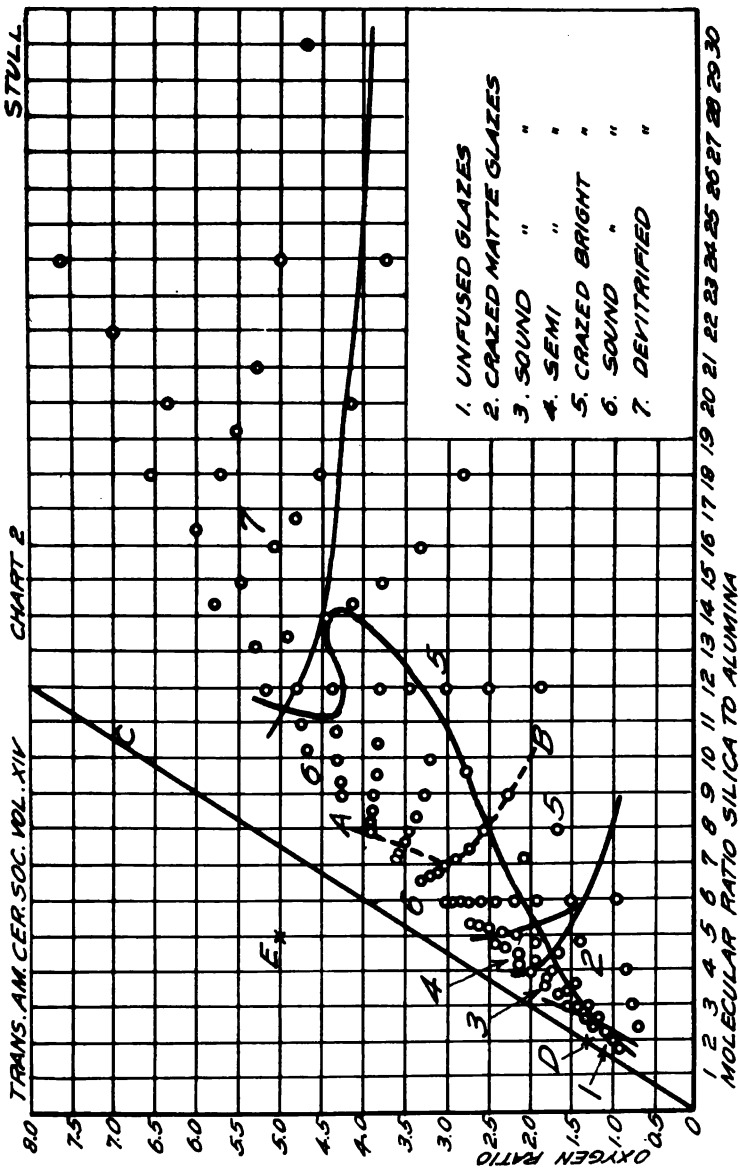

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The chart shows graphically that the matte glazes fall within narrow limits and that the bright glazes occur within wide limits. In the following table is given the ratio limits within which the different kinds occur:

	O. R.	$SiO_2 : Al_2O_3$
1. Underfired matte glazes (at cone 11)....	0.9–1.5	1.7– 2.7
2. Crazed matte glazes (at cone 11).....	0.6–1.6	2.4– 6.0
3. Sound glazes (at cone 11).....	1.4–1.9	3.0– 4.0
4. Semi-matte glazes (at cone 11).....	1.9–2.4	4.0– 5.0
5. Crazed bright glazes (at cone 11).....	1.4–4.4	6.0–24.0
6. Sound bright glazes (at cone 11).....	2.1–4.8	5.1–13.0
7. Crazed devitrified glazes (at cone 11)....	4.5–7.6	12.0–30.0

The trials show that the best bright glazes are found between oxygen ratios of 2.5 and 3.6 and silica-alumina ratios of 7 and 8.2. The best mattes occur between O. R.'s of 1.5 and 1.8 and silica-alumina ratios of 3.2 and 3.8. The high fire matte glazes given by Prof. Binns[6] fall within these limits.

As the alumina increases, the positions of the glazes approach the line passing through C to the origin O. This line represents a series of glazes having constant alumina, and variable silica. The general formula which satisfies any member in this series is RO ∞ Al_2O_3, z SiO_2 in which z may vary from 0 to ∞. When z becomes infinitely large the formula may be reduced to the simple one of 1 Al_2O_3, y SiO_2. Dehydrated kaolinite, having a total oxygen ratio of $1.3^1/_3$ and a molecular ratio of 2, is located on the line O C at D.

The line O C is the dividing line between possible and impossible glazes. Take any point to the left of this line, as point E located by an oxygen ratio of 5 and a silica-alumina ratio of 5. From the general formula of the glaze 1 RO, x Al_2O_3, y SiO_2, the following equations are obtained:

$$\frac{2y}{1 + 3x} = 5 \qquad \frac{y}{x} = 5$$

in which $x = -1$ and $y = -5$. The formula then of a glaze to be located at E must be RO, -1 Al_2O_3, -5 SiO_2 which is impossible except mathematically. In the same manner, any

[6] Trans. A. C. S., Vol. VII, pp. 115–121.

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other point to the left of O C may be shown to represent a glaze of the general formula 1 RO, x Al_2O_3, y SiO_2, in which x and y are negative.

As the dividing lines between the different glazes on Chart II approach the line O C, they curve upward, indicating that the higher the molecular content of alumina in the glaze the higher is the oxygen ratio for sound matte and bright glazes and that devitrification appears at a higher total oxygen ratio in high alumina glazes than it does in glazes lower in alumina.

The foregoing work seems to indicate that it is necessary to employ higher oxygen ratios for high alumina glazes (both bright and matte) than it is for low alumina glazes, and that the total oxygen ratio of 1 : 2 so often referred to as being best for bright glazes does not hold with, perhaps, the exception of low alumina glazes maturing at lower temperatures.

DISCUSSION WRITTEN AFTER READING THE ABOVE PAPER.

Mr. Staley: This paper is a fine example of careful and systematic work and of concise and graphic presentation of data. So well has the work been done that there is little room for discussion or comment.

From the standpoint of practical porcelain glazes, the first series, the A, B, C series, is of most interest. This may be divided into two groups of glazes: first, a group that can be made from the ordinary potter's materials, feldspar, whiting, clay and flint; and second, a group in which it is necessary to use $Al(OH)_3$, or its equivalent. The line dividing these two groups in Chart 1 runs in a straight course from the glaze with 0.3 Al_2O_3 and 1.8 SiO_2 to a point that would indicate a glaze with 1.0 Al_2O_3 and 3.2 SiO_2. It is plainly evident from the chart that the large majority of the glazes in the first group are good bright glazes at cone 11.

Inasmuch as Prof. Stull, for the sake of simplicity in blending, introduced considerable amounts of $Al(OH)_3$ into the high alumina glazes of the first group, we feel justified in predicting that if all the members of this group had been made from the materials ordinarily used by the potters. the boundaries of the matte and semi-matte areas would have been shifted somewnat toward the

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upper left-hand corner of the chart. We base this prediction on the well known fact that in high alumina glazes the introduction of a given amount of alumina as the free oxide, or its equivalent, has a more decided tendency to produce matteness than the introduction of an equal amount of alumina as clay.

Professor Stull has shown beautifully the facts that under certain conditions increase of alumina can stop crazing and increase of SiO_2 can cause crazing. Of course, both these statements are contrary to Seger.

The close relation between the boundary lines for crazing and devitrification in high silica glazes obviously suggests that the strains set up in the process of devitrification are responsible for the crazing. This is simply one more instance of crazing not caused by difference in coefficient of contraction

Inspection of the chart shows that a very simple rule can be devised for making a long series of good bright or matte porcelain glazes with this RO. Any raw glaze should have at least 0.05 equivalent of clay for mechanical reasons, so we will start with 0.35 Al_2O_3 and 2.40 SiO_2. Now by adding Al_2O_3 and SiO_2 to this glaze in the proportion of 0.10 equivalent of Al_2O_3 to 0.8 equivalent of SiO_2, we can make a long series of glazes lying close to the line of best bright glazes free from crazing. In terms of batch weights, this means that we can start with a glaze of the following batch: 33 feldspar, 14 whiting, $2^1/_2$ clay and 6 flint. To this batch we add clay and flint in the proportion of 1 part clay to 1.4 parts flint. To get the longest possible series of mattes, we simply drop out the flint from the above base glaze and make successive additions of clay. The members lowest in clay of this series would be liable to craze.

Mr. Stull: It seems to be a question as to whether all of the glaze ingredients go into solution or not. If complete solution takes place, the difference in texture of a glaze is not so marked whether the alumina has been added as $Al_2(OH)_6$ or introduced as clay. However, a high alumina content tends to increase viscosity which operates against diffusion and consequent homogeneity.

Although these matte glazes contain some alumina introduced as the hydroxide, the trials showed that the best mattes occurred

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between the O.R.'s of 1.5 and 1.8 as has been referred to. The high temperature matte glazes reported by Professor Binns in Volume VII fall within these limits. He reports his best matte as having an O. R. of 1.69. Although he used the regular potter's materials and fired at cones 8 and 9, it must be borne in mind that the replacement of clay by aluminum hydroxide and flint raises the maturing temperature. Therefore, Prof. Staley is correct in his prediction, though it is probable that the lines would have been shifted only a short distance.

The fact that increase in alumina tends to overcome crazing was, to my knowledge, first brought out by Purdy and Fox in their work on "Fritted Glazes."

A study of results plotted graphically frequently reveals far more than mere description can do. In going back to the charts, a point is observed which might be of interest to the glass manufacturer. On Chart 2 it is observed that devitrification occurs at higher oxygen ratios as the alumina increases. Since sand is the cheapest material in the glass batch, there is an advantage in using all the sand that practice will permit for common window and bottle glasses.

Frequently the manufacturer of the common grades of glass is limited in the amount of sand he can use, owing to the liability of the glass to devitrify. If alumina can be introduced or its quantity increased in the glass, a larger per cent. of sand can be employed. Not only will the alumina tend to prevent devitrification, but will also tend to counteract increased viscosity due to increased silica. The fusion temperature then would be the principal limiting factor.

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THE PLASTICITY OF CLAY.

By F. F. GROUT and FREDERICK POPPE, Minneapolis, Minn.

INTRODUCTION.

Definition of Plasticity.—Plasticity, as here spoken of, is a property developed in a clay by water, by virtue of which the clay can be molded, without crumbling, into shapes which remain stiff and unchanged after the removal of the molding force. It increases with increasing strength and with increasing capability of flowage (where flowage implies continuity of form).

Earlier Results.—The measurement and cause of plasticity were the object of a former study. Some experiments and calculations are given here in continuation of that study of the causes of plasticity. In summary, our first conclusions were: (1) That plasticity varied without definite relation to any other determinable physical property of clay. (2) That some clays are more plastic than any other mineral powder, even when in nearly the same physical condition, probably because of an attraction between clay and water, due to chemical constitution.[1] This idea will be re-stated, eliminating some inaccuracies. (3) Colloids were shown to affect plasticity. This paper reviews that work and adds new data. (4) The effects of fineness, shape of grain, and other factors were measured with care and found quantitatively insufficient to account for the plasticity, though each had some effect.[1] Little discussion has been given them recently.

The Problem.—Consider the gradual addition of water to a dry clay. The hygroscopic moisture and possibly double that amount seem to produce little change in the behavior of the clay powder. With ten or twelve per cent. water, some clays will form a very stiff mud, requiring high pressure for molding and allowing only slight flowage without fracture. If more and more water is added, the clay becomes gradually softer, until it flows as a thin liquid and has no measurable strength. Between these two points, both strength and flowage are measurable, and plasticity possesses a maximum. The addition of water, or a similar liquid, is essential and must be considered as of prime

[1] F. F. Grout, Jour. Amer. Chem. Soc., XXVII, 1046.

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importance as a cause of plasticity; but since water does not make other mineral powder equally plastic we must seek farther.

Plasticity being a double property, involving both capability of flowage and strength, must have a cause that will explain both factors. In a wet clay, the flowage is commonly and correctly considered as explained by the lubricating action of the water between the grains. Water is so clearly fluid that we all expect and know that the addition of a considerable quantity to any fine powder makes that powder somewhat more fluid. This factor being clear, there remains to be explained the cause of the strength of the wet mass. Something must render the water viscous, so that the clay resists flowage, except under rather great pressure, when wet enough to be well lubricated. Common dilute solutions and suspensions are not viscous enough. Only two explanations are well supported: that of molecular attraction, and that of colloidal solutions.

THE MOLECULAR ATTRACTION THEORY OF PLASTICITY.[2]

Every solid particle wet by water has over its surface a thin film of water bound to it by such strong attraction that it becomes viscous. The friction of moving water at the contact is said to be infinite as compared to that in water outside the film. The strong attraction, however, has not been detected at a distance of more than about 0.00005 mm. from the contact surface and would seem to involve a very inconsiderable amount of water until one recalls the minute size of clay grains. Calculation will be given to illustrate this. The essential fact in the theory is that *the attraction varies with the nature of the substances.* If attraction is stronger in clay than in other powders, a *thicker film* will be bound and rendered *more viscous* than by other powders; and so the wet clay will be more plastic. The range of attraction is so small that no method has been devised for showing variations for the different substances, but such variations are constantly assumed by the physicists.

[2] The original statement of this idea has been criticized, and the present statement improved by Ross C. Purdy, Ill. Geol. Survey, Bull. 9; H. Ries, "Clays, Properties, Occurrence and Uses," Wiley & Sons; and H. E. Ashley, U. S. Geol. Survey, Bull. 388.

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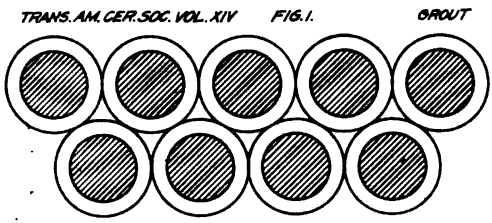
The adequacy of the idea is questioned by Purdy[3] who presents a calculation to show that in most clays much water is used besides what is needed for films. It is well to think out carefully the relations of grains, films and pore spaces. Pore space in clay varies widely, records showing 18 to 31 per cent. Theoretically, uniform spherical grains always have over 25 per cent. pore space. In an actual clay, King found a pore space as high as 48 per cent.[4] In state survey reports, we find Illinois clays range from 23 to 28 per cent., Iowa clays from 18 to 31 per cent., West Virginia clays from 23 to 30 per cent. Evidently the lack of uniformity in size of grain is balanced by the angularity and lack of a compact arrangement of grains, so that a pore space of 25 per cent. is a good, conservative average.

Next, consider the effect of adding a film of water around each grain, just thick enough to be rendered viscous. It is not suggested that water added to clay usually forms such films before filling the pore space; just the reverse. But for clarity of ideas consider, now, each grain as enlarged by the addition of



this film 0.00005 mm. thick on all sides. The grains would tend to be more uniform rather than less uniform in size. There is no reason to think that these enlarged grains would be arranged in such a way as to cause any reduction in per cent. of pore space. The enlarged grains, packed so as to touch their neighbors on several sides, would still have 25 per cent. pore space. This could be filled with water without separating the grains any farther; that is, even with the addition of 25 per cent. by volume of water, the grains would still be so close together that viscous

[3] Ill. Geol. Survey, Bull. 9, p. 176.
[4] U. S. Geol. Survey, 19th Annual Report, Part 2, p. 208.

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films would be in contact between each grain and its neighbor. There would be resistance to flowage, after addition of water enough to fill both pores and films.

Now a calculation of water needed for films and pores must be based on some assumptions. For the size of grains I use the mechanical analyses. (First assumption.) One might assume numerous observations that clay grains are plate-like in form, but as this gives a large proportion of film and pore space it might be more conservative to assume half spherical and half plate-like, with breadth five times as great as thickness. (Second assumption.) The pore space is 25 per cent. (Third assumption.) The specific gravity of clay is 2.7.

CALCULATION OF THEORETICAL "WATER OF PLASTICITY."

Stated in terms of per cents. of dry clay, and calculated for several sizes of grains.

I. For Spherical Grains Less than 0.001 mm. in Diameter.

The average diameter of dry grains is 0.0005 mm.

The average diameter of grains enlarged by water films is 0.0006 mm.

The volume of a dry grain is $\frac{\pi D^3}{6} = \frac{\pi(0.0005)^3}{6}$ cubic mm.

The volume of the enlarged grain is $\frac{\pi(0.0006)^3}{6}$ = cubic mm.

Ratio of original volume to enlarged volume is $\frac{(0.0005)^3}{(0.0006)^3} = \frac{125}{216}$.

That is, 125 volumes of clay bind 91 columns of water in viscous films.

Now if the grains, enlarged by films to a volume of 216 units, were packed as closely as possible without thinning the films, there would still be a large pore space which we may assume to be 25 per cent. of the whole, the enlarged clay grains occupying 75 per cent. of the whole.

If 216 units of volume are 75 per cent., 100 per cent., or the whole volume of clay, films, and pore space, is $\frac{100}{75}$ of 216 = 288 units volume.

The volume ratio of clay to (clay + film + pore) is $\frac{125}{288}$.

The ratio of clay to (film + pore) is $\frac{125}{163}$.

This means that in the case suggested more volume is occupied by water than clay; but if we assume that clay has a specific gravity of 2.7, the 125 units of clay by volume represent 337.5 units by weight and 163 units of water by volume represent 163 units by weight.

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The addition of 163 parts by weight of water to 337.5 parts by weight of clay is an addition of 48.3 per cent. of the weight of the dry clay. This is the requirement for films and pores in spherical grains below 0.001 mm. in diameter.

II. Small Plate-like Grains.

Abbreviating the calculation for plate-like grains, we may assume the original grain to be $0.0005 \times 0.0005 \times 0.0001$.

The enlarged clay grain would be $0.0006 \times 0.0006 \times 0.0002$ mm.

The volume ratio would be $\frac{25}{72}$. The ratio $\frac{\text{Clay}}{\text{Water}} \frac{25}{47}$.

Similarly, considering a pore space of 25 per cent. still to be filled, we find the ratio of clay volume to (film + pore) volume to be $\frac{25}{71}$.

Again, assuming that the specific gravity of clay is 2.7, we can calculate per cents.

The per cent. of water for films and pores is 104 per cent.

III. Large Spherical Grains.

With larger grains the standard size is 0.001–0.005 mm. but Mr. Purdy in Illinois University selected a size 0.001–0.01 mm., and the calculation may be made for grains as he wants them.

The original diameter may be assumed 0.005 mm.

The enlarged diameter is then 0.0051 mm.

For spherical grains the volume ratio is $\frac{125}{132.65}$.

The ratio $\frac{\text{Clay}}{\text{Water}}$ by volume is $\frac{125}{7.65}$.

With water added to fill the pores 15.3 per cent. water is required.

IV. Large Plate-like Grains.

For plate-like grains the following serves:

Original dimensions $0.005 \times 0.005 \times 0.001$.

Enlarged by films $0.0051 \times 0.0051 \times 0.0011$.

The volume ratio $\frac{\text{Clay}}{\text{Water}} = \frac{25}{3.6}$.

With water added to fill pores 19.7 per cent. water is required.

Some allowance may be made especially for pore spaces in still larger grains, if they constitute a high per cent. of the whole.

From this it is seen that for grains less than 0.001 mm. in diameter, an average of about 75 per cent. water is required. For grains below 0.01 mm., an average of about 18 per cent. water is required. In twenty Illinois clays reported by the state survey, the average water used was 15.8 per cent.; that

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calculated for films and pores was 16.3 per cent. Similar results are obtained from Iowa and West Virginia clays where analyses were available. Now while these averages are very close, the variation in particular cases needs explanation. Two points may be mentioned. First, clays vary in the shape of grain, and our assumption may be wrong in particular cases. Second, the per cent. of water needed, as reported in these bulletins, is determined by a man's opinion, and not by a mechanical test of the plasticity.

However, the space here devoted to the calculation may give the matter undue prominence. There is no doubt that viscosity in these films is very great at the contact. Also, it is clear that the viscosity decreases very rapidly with distance, as it is inappreciable at a distance much over 0.00005 mm. The point to emphasize is that *for some distance, no matter what, the film is viscous, and the thickness and the viscosity vary with the substances used.*

There may be some question, as to the justice of assuming that the films spread to all sides of the grain. Consider the water between the solid particles as having a greater attraction for clay than the clay has for clay. More water particles will be drawn in between the clay grains (as long as there is a supply) until the water covers all sides of the clay to a thickness equal to the range of molecular attraction. There is a tendency for grains to separate—deflocculation. On the other hand, if the clay grain attracts its neighbor more strongly than it does water, the clay grains will crowd out the water and draw together —flocculation. Salts present in the water affect the attraction, as can be easily shown in dilute suspensions. Some salts and concentrations cause flocculation, some deflocculation. In the Illinois Geological Survey, Bulletin 9 (page 189), Purdy discusses this matter (speaking of "potential" which he does not define or use clearly). He implies that potential, surface tension, and surface pressure have a greater range of activity than molecular attraction, but they are really manifestations of the same force.

The particular salts present in the water of a plastic clay are not well studied. Mr. Purdy argues that salts *adsorbed*

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by kaolin are the cause of deflocculation and thereby of plasticity. But his logic is not good. He quotes Bourry: "Kaolins do not retain more than 2 per cent. of carbonate of lime in solution while plastic clays can absorb from 10 to 20 per cent. of it." Mr. Purdy claims that the cause of plasticity is salts *adsorbed*, but proceeds to show that the more plastic a clay is the *more ability* it has to adsorb salts. If both were true, the adsorption and plasticity would both soon be infinite. If the salts caused the plasticity of Bourry's clay, it would be *less* capable of adsorbing more salts than the lean kaolin. Again it is hard to conceive of the formation of a kaolin without production of all the salts needed. Purdy speaks of salts being washed away in the formation of kaolin, but shows that when a kaloin has been in contact with certain salts they cannot be washed away. The whole matter of adsorption was questioned from a scientific study, even before Mr. Purdy's proposal was published,[5] and as adsorbed salts are seldom the only ones present it seems best to omit that complexity and simply recognize the fact that the solution is variable. The molecular attraction will then vary, both with the nature of the solid and with the nature of the solution. It is frankly admitted that if such attraction is the basis of plasticity of clays, it is an extraordinary attraction, stronger than is found in other minerals.

THE COLLOID THEORY OF PLASTICITY.

Earlier work has shown quite definitely that the addition of colloids to a fine powder increased its plasticity. Colloids are so manifoldly variable in their properties that the discussion is in a state of extreme confusion. Since colloids can increase plasticity, it became of interest to determine their presence or absence in clays. The methods used are direct and indirect. Some are applicable to the discussion of plasticity and some are not. Ries[6] gives an excellent summary of the present state of the discussion. Very recent and elaborate experimental work was done by Stremme and Aarnio,[7] without special reference to the study of plasticity. The direct methods are solution

[5] U. S. Geol. Survey, Bull. 312, page 64.
[6] "Clay, Occurrence, Properties and Uses," 1906, pages 99–103.
[7] Zeit. Prakt. Geol., XIX, 329.

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methods involving in various cases acids or alkalies, or both. The indirect methods involve an assumed relation between colloids and some physical property such as hydrolysis, osmosis, adsorption of salts and dyes, change from sol to gel form, shrinkage, and vapor tension. Stremme and Aarnio made a comparative study of the direct or solution method, Ashley's method of adsorption of dye, and Rodewald-Mitscherlich's hygroscopicity method. They concluded that the last was the best measure of colloids as developed by rock decomposition.

Attention being limited to those colloids which are related to plasticity, it is to be emphasized that the indirect and some direct methods measure colloids of other kinds. Silicic acid, when evaporated to form jelly, becomes viscous enough to affect plasticity. If this same solution is evaporated to dryness, it forms a glassy mass which acts like quartz sand in that it injures rather than improves plasticity. Yet it still takes an organic stain, very strongly. A short series of tests indicated[8] that inorganic colloids all behaved as silicic acid, but that organic colloids, like gelatine, were capable of increasing plasticity, even after evaporation to dryness. Ashley threw doubt upon the conclusion by suggesting that probably the inorganic colloids would have returned to their active condition if time had been longer or if the mass had been ground wet. He did not report doing so. We have not succeeded. A most important fact is that clays do not need this long time or wet grinding to show notably high plasticity. We, therefore, emphasize the fact that some colloids have no beneficial effect on plasticity and would question still further if any inorganic colloid can explain the effects found in clay. Indirect methods do not distinguish these two classes of colloids. Direct methods have not been well tested with this in mind. Nearly all the discussion of recent years, when thus simmered down, is based on a single test made by Th. Schloessing nearly forty years ago. The recent work on extraction of silica from clays by use of sodium carbonate[9] may prove of value, but its bearing is still uncertain.

[8] W. Va. Geol. Survey, III.
[9] F. K. Pence, Trans. A. C. S., XII, 43–53.

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Schloessing[10] washed 40 grams of clay with acid and then suspended it in slightly ammoniacal water and allowed it to stand 27 days. There remained 0.59 gram in the clear supernatant liquid with the properties of a colloid and composition almost like a clay.

We have selected some notably plastic clays for further experiments as follows:

(1) 150 grams were wet, molded, dried, extracted with warm water and filtered warm. The filtrate was evaporated, very slowly toward the end, but no colloid was found.

(2) The process was repeated with a modification in the first wetting, where agar-agar solution was used instead of water. The amount of agar added was 0.2 per cent. of the weight of the clay. In the final evaporation, the extract set to a very firm jelly, indicating that such organic colloids could be extracted by hot water.[11]

(3) Since this method of simple hot water extraction failed to reveal colloids in a natural clay, it was thought that Schloessing's treatment would best be followed in detail, but it was found that he did not report the detail of his method very fully. In the attempt to follow his work, 40 grams of plastic "Dakota" fire clay from northern Colorado were digested an hour in 5 per cent. hydrochloric acid, filtered, and washed with distilled water for six hours till most of the acid was removed. The clay was then suspended in 500 cc. of water with an addition of about 5 cc. ammonia (sp. gr. 0.9) and shaken thoroughly. After 27 days (the time given by Schloessing), not enough had settled clear to allow a test. The centrifuge did not help. After six months, a portion was removed and allowed to evaporate. The residue had the horny translucent appearance of a colloid. It cracked and was quite hard and adhered strongly to the dish, but it became soft very promptly when wet with water, even after thorough drying. The dry weight of colloid and any other matter from the solution was 1.47 grams from 40 grams clay. The color was brown, indicating either organic matter or ferric

[10] Compt. Rend , LXIX, 376, 473 (1874).

[11] In previous work in this line reported in the West Va. Geol. Survey, Vol. III, we used a porcelain filter and found no colloid.

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colloid. Ignition gave an odor of organic matter, but the loss was only 0.27 gram, showing that the matter was largely inorganic. The ignited mass was colored by some iron compound.

(4) A duplicate was treated in the same way as (3) with the omission of acid extraction. The colloidal matter was approximately one-fourth as great.

(5) A portion of the clear solution of each of the last experiments was evaporated to dryness, wet with an excess of water, filtered, and again evaporated to determine whether the colloid found would dissolve in *water*, after having been obtained by use of *ammonia*. About half of it went promptly into solution and when dry, again behaved as a colloid.

The interpretation of these results is not easy. Schloessing was evidently correct in reporting colloids present. We all knew they were present. But *to find a colloid which will soften when wet, it was necessary to use alkali*, or both acid and alkali. These are not needed to make a clay plastic; pure water is sufficient. Still it is not unreasonable to think that some colloidal matter may be in the final form found in the last experiment—capable of softening but not dissolving without long standing in ammoniacal water. We find no reference to a detailed description of such a colloid in the literature, but it seems to exist.

It is noteworthy that the beneficial effects of colloids are not limited to plasticity but are to be studied in tensile strength of dry clay.

As a final argument let us call attention to the fact that using the finest powder obtainable from other minerals, with the most active colloids known, we have not succeeded in making that powder as plastic as common clay. If some one will find a more active inorganic colloid or succeed in making some non-plastic powder as plastic as clay by the use of colloids, the theory will be more acceptable. While our short series of tests failed, a longer series might change the conclusion. For the present we consider colloids a minor factor in the production of plasticity in clays.

SUMMARY.

In summary, we find that the essential peculiarity of a plastic clay is the fact that the water used in wetting the clay is somehow

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rendered viscous. In explanation we have two well known phenomena: molecular attraction and the action of colloids. Both are certainly present. Both are necessarily active. The calculation indicates that molecular attraction may be quantitatively sufficient, especially since the force is known to be variable and may be greater in clays than in any other mineral. Colloids alone would probably be quantitatively insufficient. No experiments have shown them capable of such effects in other mineral powders.

DISCUSSION.

Mr. Purdy: Again I say, "I told you so." The arguments presented by Mr. Grout are, with one exception, exactly those that I have been presenting to this society on several occasions; that one exception is adsorbed salts. Mr. Grout goes with me up to that point. I never denied the presence of colloids in clays, but I have doubted the possibility of these colloids producing plasticity. Regarding the adsorption proposition, I think he will agree with me that in this clay is usually most peculiar; there is no other mixture that will show the adsorbent property that clay will and that is the reason I have thought that the adsorption was a factor, and I still do for that matter. Mere similarity in fineness of grain will not permit these volumes of water to cause plasticity—those grains must have a peculiar property and the only peculiar property that is distinctly that of clay is this strong absorption and for that reason I link that into the argument.

Mr. Grout: Since plasticity is a very peculiar property, characteristic of clay, it is not quite correct to say that the strong adsorption is the only peculiar property distinctly that of clay. They are both noteworthy and almost unique, and they may even be due to the action of the same forces; but there is no more evidence that adsorption causes plasticity than that plasticity causes adsorption.

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RESULTS OF TESTS ON SOME BRICKS FROM THE PROVINCES OF WESTERN CANADA.

By HEINRICH RIES, Ithaca, N. Y.[1]

Introduction.—The rapidly growing towns and cities of the Canadian West have called for considerable building material, and since lumber in many parts of the Great Plains is high-priced, brick is often selected. This demand has naturally stimulated the development of brick yards, and not a few are now in operation in Manitoba, Saskatchewan, Alberta and British Columbia.

The Samples.—During the work on the clays of Western Canada,[2] a number of sets of bricks were collected from the different yards, for testing purposes. As far as possible normally burned bricks were chosen, and wherever it could be done, the samples were picked from the kiln.

The Tests.—These were then shipped to Kingston, Ont., and were tested by Prof. A. McPhail, of the School of Mines, in accordance with the printed recommendations of the Committee on Testing Brick appointed by the American Society for Testing Materials. Sixteen sets in all were tested, the individual tests published representing the average of 6.

The accompanying tables, which are almost self-explanatory, give: I, the character of the raw material and method of manufacture; II, absorption, transverse and crushing tests; III, freezing tests.

Discussion of the Results.—A comparison of the figures shown in these tables is not without interest.

Considering the entire series of tests without regard to the method of manufacture, the following facts are observable: The absorption ranges from 10.5 per cent. to 25.8 per cent., and half of those tested show an average absorption of over 20 per cent., but while none of those of high absorption show a high crushing strength, not all of those with the lower absorption show a high figure for the crushing test.

The transverse strength is usually good, but in only ten of the sixteen sets did the transverse strength of the wet brick average

[1] Published by permission of the Director, Canadian Geological Survey.

[2] H. Ries and J. Keele, Canadian Geological Survey, Memoir 24 E, Ottawa, 1912.

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TABLE I.—CHARACTER OF RAW MATERIAL AND METHOD OF MANUFACTURE.

Series No.	Material used	Method of manufacture
A	Shale	Dry press
B	Calcareous surface clay	Soft mud
C	Calcareous surface clay	Soft mud
D	Niobrara shale	Dry press
E	Calcareous, silty, surface clay	Soft mud
F	Calcareous glacial clay	Stiff mud
G	Silty, flood plain clay	Dry press
H	Silty, flood plain clay	Stiff mud
I	Silty, flood plain clay	Soft mud
J	Silty surface clay	Soft mud
K	Silty surface clay	Soft mud
L	Cretaceous shale	Stiff mud
M	Cretaceous shale	Dry press
N	Cretaceous shale	Dry press
O	Surface clay, sandy	Soft mud
P	Surface clay, sandy	Soft mud

lower than that of the dry one. In four other cases it was practically the same.

Comparing the crushing test flat (dry) with the crushing test on edge (dry) there seems to be no constant increase or decrease, for in seven cases the crushing strength on edge is less, and in the other cases it is greater.

The tests bring out well the inferiority of the bricks made from too sandy surface clays.

If some of these clays were burned a little harder the product would be stronger.

Comparing the crushing strength on edge dry with the crushing strength on edge wet, it was found that in ten of the sixteen series the water-soaked ones were weaker.

In only seven cases was the crushing strength of the bricks which had been through the frost test less than that of the bricks not so treated.

Grouping the tests according to methods of manufacture shows that in the series tested: (*a*) the dry press brick average lower in absorption, probably because they are made of denser

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TABLE II.—ABSORPTION, TRANSVERSE AND CRUSHING TESTS.

Series No.	Test A	Test B. Transverse (dry)		Test C. Transverse (wet)		Test D. Crushing	Test E. Crushing	Test F. Crushing	Test H. Crushing
	Per cent. absorption	Breaking load	Modulus of rupture	Breaking load	Modulus of rupture	Flat (dry), lbs. per sq. in.	On edge (dry), lbs. per sq. in.	On edge (wet), lbs. per sq. in.	On edge (dry), after freezing, lbs. per sq. in.
A.....	13.5	1533	805	1490	773	6975	5960	5132	4700
B.....	23.2	887	472	843	472	2208	2358	1547	2196
C.....	22.1	1150	647	1073	594	2435	2567	1983	3260
D.....	10.5	1295	622	1273	610	2807	2652	2833	3378
E.....	23.1	983	473	1432	716	1830	2468	2310	2846
F.....	25.8	1286	746	977	568	2932	2050	2065	1730
G.....	25.5	704	337	720	345	2612	1744	1562	1250
H.....	19.2	825	384	920	428	1692	1868	1628	2027
I.....	22.2	702	365	617	320	1298	1512	1282	1400
J.....	24.1	774	337	797	343	1220	1492	1502	1989
K.....	15.8	640	298	506	237	1320	1494	1310	1732
L.....	14.4	672	313	598	278	2242	1660	1948	1950
M.....	15.3	657	267	612	249	2343	1364	1513	1503
N.....	15.8	808	329	662	270	2420	1640	1296	1190
O.....	20.8	972	467	983	471	1869	1950	2658	1990
P.....	14.4	2008	972	1618	776	5242	5735	4028	5115

burning clays or shales; (*b*) many of the soft mud brick show a high percentage of absorption, largely because they are made of very sandy surface clays; (*c*) all three groups show a considerable range in their modulus of rupture; (*d*) the soft mud and dry press bricks show a higher maximum crushing strength than the stiff mud, but this is due certainly to the raw materials rather than the process.

Table III containing the results of the frost tests is equally interesting, for it will be recalled that in accordance with the recommendations of the American Society for Testing Materials these had to be frozen and thawed 20 times. It was not the strongest bricks nor the denser ones that stood up best in the frost test, as brought out by Series C and H.

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TABLE III—FREEZING TESTS.

Series A		Series B		Series C		Series D	
No.	Remarks	No.	Remarks	No.	Remarks	No.	Remarks
1	8 cracked, 15 broken[1]	1	5 cracked, 14 broken	1	20 cracked	1	16 broken
2	11 cracked, 15 broken	2		2		2	16 broken
3	8 cracked, 15 broken	3	5 slightly cracked	3		3	
4		4		4		4	16 slightly cracked
5		5		5		5	
		6	5 slight scaling	6		6	
	Series E		**Series F**		**Series G**		**Series H**
1	8 scaling, 20 broken	1	20 scaling	1	2 cracked, 8 broken	1	
2		2	16 broken	2	2 cracked, 8 broken	2	
3		3	3 scaling, 16 broken	3	2 cracked, 16 broken	3	
4		4		4	2 cracked, 16 broken	4	
5	5 cracked	5		5	2 cracked	5	
6		6	5 scaling, 8 cracked	6	2 cracked	6	
	Series I		**Series J**		**Series K**		**Series L**
1	8 scaling	1	3 scaling	1	8 scaling	1	2 cracked
2		2		2		2	8 cracked
3		3		3	2 scaling	3	8 cracked
4		4		4	8 scaling	4	8 cracked
5		5		5		5	2 cracked
6		6	5 scaling	6		6	
	Series M		**Series N**		**Series O**		**Series P**
1	2 cracked, 8 large cracks	1	7 crumbled	1	20 broken	1	16 broken
2	2 cracked, 8 crumbled	2	16 crumbled	2		2	8 corner cracked
3	2 cracked, 8 crumbled	3	7 crumbled	3		3	8 cracked and blistered
4	2 cracked, 16 crumbled	4	11 cracked	4	16 crumbled	4	16 cracked, 20 broken
5	8 cracked, 11 large cracks	5	8 crumbled	5	20 broken	5	8 cracked, 15 broken
6	8 cracked, 16 large cracks	6		6	12 corner crumbling	6	

[1] The [illegible]

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If we take the percentage values assigned by Prof. McPhail to each for the freezing test and arrange the brick in this order with their corresponding absorptions, we see that the lack of relation between absorption and frost resistance is not determined by absorption alone.

Series No.	Rating. Per cent.	Absorption. Per cent.	Series No.	Rating. Per cent.	Absorption. Per cent.
H.....	100.0	19.2	A.....	64.0	13.5
C.....	99.5	22.1	B.....	60.0	23.2
I.....	89.5	22.2	P.....	59.0	14.4
D.....	87.5	10.5	K.....	55.0	15.8
O.....	87.0	20.8	N.....	44.0	15.3
E.....	76.0	23.1	L.....	33.0	14.4
J.....	71.5	24.1	M.....	15.0	15.3
F.....	66.5	25.8	G.....	5.0	25.0

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SOME DATA ON THE DEFORMATION POINTS OF FELDSPAR-QUARTZ, FELDSPAR-MICA, AND FELDSPAR-BERYL MIXTURES.[1]

By A. S. WATTS, Washington, D. C.

FELDSPAR-QUARTZ.

The presence of quartz in feldspar offered for sale has long been considered unpermissible, even though the user expected to add quartz to the mixture later. This stand was taken because of the fear that the feldspar would be adulterated to the extent that its solvent action would be seriously reduced. The impression has also prevailed that even small additions of quartz to feldspar would greatly increase the heat treatment necessary in order to bring the mass into a liquid state. As exact data on this subject was absolutely lacking, the writer carried on an investigation with additions of pure quartz to a pure microcline feldspar.[2] These materials were ground separately to pass a

	Analysis of feldspar. Per cent.	Theoretical microcline. Per cent.
Moisture	0.17	
SiO_2	65.37	64.75
Al_2O_3	17.92	18.34
TiO_2	trace	
Fe_2O_3	0.02	
CaO	0.17	
MgO	trace	
K_2O	13.05	16.90
Na_2O	2.10	
	98.80	99.99

200-mesh screen. They were then ground together until thoroughly mixed and made into cones similar to the pyrometric cones of commerce against which they were to be tested. The following is the record of the test burn:

The test kiln is an up-draft kiln with a muffle 7″ × 8″ × 18″ deep. Gas is the fuel and an even temperature throughout can be maintained by slow and careful increase of gas pressure. Twenty hours were consumed in reaching cone 7 temperature, *i. e.*, 1270° C. Eight hours additional were consumed in raising the temperature to cone 9, *i. e.*, temperature 1310° C.

[1] By permission—U. S. Bureau of Mines.

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With the rate of deformation of cone 8 (1290° C.) and cone 9 (1310° C.) as standards, a diagram is given herewith showing the relative temperatures and speed of deformation of the various mixtures of feldspar and quartz up to and including 35 per cent. quartz (see Fig. 1).

TRANS. AM. CER. SOC. VOL. XIV FIG. 1. WATTS

DEFORMATION STUDIES

FELDSPAR-QUARTZ SERIES

			F	A1	A2	A3	A4	A5	A6	A7
	FELDSPAR - 100 QUARTZ - 0			95 5	90 10	85 15	80 20	75 25	70 30	65 35
8g	Cone 8	Cone 9								
8f										
8e										
8d										
8c										
8b										
8a										
8										
9f										
9e				Down	Down					
9d	Down		Down	"	"					
9c	"		"	"	"					
9b	"		"	"	"					
9a	"		"	"	"		Down			
9	"		"	"	"	Down	"			

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Thus we see that even though 30 per cent. of the mixture is quartz the deformation temperature is raised less than two cones or 40° C. This is not in accordance with the work of Simonis[2] who found that a mixture of 70 per cent. feldspar and 30 per cent. quartz had a deformation temperature of cone 14, 1410° C., which is about 100° C. higher than his pure feldspar deformation point. This difference in results can be accounted for only by assuming that the feldspar used in the Simonis tests carried some free quartz and thus the further additions of quartz made the deformation point unduly high.

The important point brought out by this investigation is the fact that the user cannot be certain that he is obtaining pure feldspar by testing the material alone in the kiln. A mixture of 95 per cent. feldspar and 5 per cent. quartz begins to deform at the same temperature as pure feldspar, but becomes fluid much quicker than does pure feldspar. A mixture of 90 per cent. feldspar and 10 per cent. quartz deforms at a temperature approximately 5° C. higher than does pure feldspar but becomes liquid before the pure feldspar has begun to lose shape.

No eutectic indications are noticeable in the original fusion of feldspar-quartz mixtures, unless we so construe the fact that the 95 per cent. feldspar-5 quartz mixture began deforming when the feldspar began and completed deformation ahead of the pure feldspar. To determine if there is any eutectic indication in feldspar-quartz fusions, mixtures of pure feldspar and quartz were fused together in the above proportions, and after reducing the fusions to 200-mesh powders they were made into cones which were tested against standard pyrometric cones as before.

The same order of fusibility is noted in this firing as was recorded in the firing of the raw mixtures. F and A begin to deform at cone 5, 1230° C., but as was noted in the firing of the raw mixtures, A 1 deforms more rapidly and touches the plate when F is only half down. A 2 begins to deform after F and A1 have started but overtakes F when nearing the plate. F 3, 4, 5, 6, deform in regular order. A 7 was an imperfect cone and no reliable reading could be made on it, but A 6 was deformed so that it touched the plate before cone 7 started to deform.

[2] Sprechsaal, 1907, No. 30, pp. 403–6.

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TRANS. AM. CER. SOC. VOL. XIV FIG. 2 WATTS

DEFORMATION STUDIES

FELDSPAR-BERYL SERIES

		F	D1	D2	D3	D4	D
FELDSPAR		100	95	90	85	80	0
BERYL		0	5	10	15	20	100
Cone 6	Cone 7						
Down							
Down							
Down							

FELDSPAR-MUSCOVITE SERIES

		F	C1	C2	C3	C4
FELDSPAR		100	95	90	85	80
MUSCOVITE		0	5	10	15	20
Cone 7	Cone 8					
Down						

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FELDSPAR-MUSCOVITE.

As muscovite is present in nearly every feldspar, it is important that we know what influence it exerts on the deformation point and color of the feldspar. For this purpose a series was made up of feldspar-muscovite mixtures and tested in the manner just described with regard to the feldspar-quartz mixtures. The muscovite was ground to pass a 200-mesh sieve, and the feldspar was of the same fineness. The table showing the results of this test is given in Fig. 2. It is especially interesting in view of the fact that muscovite has a composition $K_2O\ 3Al_2O_3\ 6SiO_2\ 2H_2O$, containing the same elements as feldspar, but by virtue of its higher Al_2O_3 content, being more difficultly fusible. It is reported by Rieke as deforming with cone 13.

In the table, you will note that C 1, containing 5 per cent. of muscovite, begins to deform before any other mixture tested. The order in which the various mixtures deform is regular, C 4 being the last to begin to deform. The rate of deformation, however, appears to be just the reverse of this, since C 4 deforms until it touches the plate before any other of the series. Note also that as C 1, which has the slowest rate of deformation, touches the plaque, F, which is pure feldspar, shows the first indication of deformation. Thus it appears that additions of finely ground muscovite to a microcline feldspar lowers the deformation temperature, and the rate of deformation increases with the increase in muscovite.

The influence of muscovite upon the color of the feldspar is really the most important consideration. The amount present would hardly be sufficient to average one per cent. in any deposit known. The difference in color is scarcely detectable when a mixture containing 5 per cent. of muscovite is brought side by side with the pure feldspar. In any event, the tint produced is a pale drab which is the same as is imparted to porcelains by the ball clay and hence would not be noticed.

FELDSPAR-BERYL.

The presence of crystals of beryl in the pegmatite dykes and the fact that they are found chiefly associated with the portions richest in feldspar demand that we ascertain what influence this mineral exerts upon the feldspar.

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For this purpose, a series of mixtures of microcline and beryl was prepared, ground to 200-mesh fineness and made into cones. These cones were tested in the same manner as were the feldspar-quartz and feldspar-muscovite mixtures (see Fig. 2).

Beryl has a mineral composition: $3GlO\ Al_2O_3\ 6SiO$. GlO may be replaced by Na_2O, Li_2O, Cs, or H_2O.

The first of this series to deform is D 4, which begins to deform as cone 6 touches the plate. The mixtures D 3, D 2 and D 1 follow quickly after the D 4. The feldspar-beryl series continue to deform in the order in which they start, the first to begin deforming being the first to touch the plate, etc. The entire series deforms completely within less than one cone temperature range, starting at cone 6 touching, and extending to cone 7 not quite touching the plate. This series indicates that the deformation temperature decreases with increase of beryl content, at least to 20 per cent., where the series ended. As a test cone of pure beryl was tested with this series and was heated up to cone 8 without deforming, a eutectic is indicated between feldspar and beryl. A study of the fired cones indicates slightly more deformation in the D 3 mixture, but as this was not apparent in the process of deformation its influence is difficult to determine.

DISCUSSION.

Mr. Mayer: What did you say about regrinding after the cones were once melted?

Mr. Watts: In the feldspar-quartz series, I took the cones that I had once tested, ground each one separately to two hundred-mesh fineness, and worked this up into other cones and tested them over again. I found that they melted uniformly two cones lower than the first time that the material was tested.

Prof. Bleininger: There are a number of valuable points in this paper. The time has arrived when we must know more about our American raw materials, and it seems to me that it is extremely important that this work has begun, and is now under way. We, perhaps, do not realize the importance of the work which Mr. Watts has undertaken; but it is bound to be of great value with reference to the development of our clay resources.

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Mr. Minneman: Do I understand you to say that pure feldspar was used?

Mr. Watts: It is pure microcline feldspar so far as the mineralogist and chemist could determine.

Mr. Minneman: It was simply a picked hand sample?

Mr. Watts: Yes. In the preparation of it, I may explain, it was first broken into particles about the size of a pinhead, and then all gone over with a hand glass to determine the presence of any particles of quartz or mica which might be there. These were all taken out, so that the material which you have here in this investigation is all absolutely pure microcline; that is what we have been calling orthoclase. I have some specimens of orthoclase; also specimens of microcline. Impurities are always present in hand samples of these minerals in more or less amount, and it was necessary that I should take the crystalline material as pure as I could get it, and break it into small pieces, which, as far as could be determined, were pure.

As evidence that they were pure, the analysis I had made shows absolutely no free silica; according to this analysis there would be about 0.7 per cent. of silica lacking, if we were to calculate the potash and soda feldspar formulae, as we are accustomed to calculate these different feldspars.

If there was a eutectic there it would be found in some place through this series; if there is a eutectic any place it is only with the 5 per cent. of quartz and the 95 per cent. of feldspar, that is as indicated by the data here compiled.

Prof. Staley: I simply want to emphasize one point. We must understand that Mr. Watts has brought out the fact that there is no deformation eutectic at any mixture of feldspar and quartz; he has not developed the fact that there is no melting-point eutectic between feldspar and quartz. The true melting-point line for mixtures of feldspar and quartz, that is the line showing the temperature at which such mixtures lose their crystalline character, still remains as shown by Vogt.[3] There is a true melting-point eutectic between feldspar and quartz at 75 per cent. feldspar and 25 per cent. quartz; but as shown by

[3] Die Silikatschmellösungen, Part II, page 127.

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Mr. Watts, there is no deformation eutectic at any point in mixtures of these two minerals. The difference between these two kinds of eutectics was discussed in a paper I presented to the society last year.[4]

Mr. Watts: This is not the melting-point eutectic; this is a case of deformation eutectic; it is a new word, which the lay potter and others must use in speaking of melting; we cannot say melting any more because the physical chemists have given another meaning to the word.

[4] "Melting-Point and Deformation Eutectics," Trans. A. C. S., Vol. VIII, page 668.

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A STUDY OF GLAZE COMPOSITION ON THE BASIS OF "NORMS."[1]

By Ross C. Purdy, Columbus, O.

INTRODUCTION.

Bristol glazes are derivatives from the porcelain glazes, the formulae of which are similar to those of the Seger cones. In researches on Bristol glazes, however, it has been developed that it is impossible to make a commercially successful Bristol glaze on the cone 4 formula, notwithstanding the fact that soft porcelain glazes, such as are used on electrical insulators, are often made by merely substituting ZnO for a portion of the CaO in cone 4. Even in these glazes, however, the equivalent contents of Al_2O_3 and SiO_2 are generally varied from those in cone 4. To produce an opaque Bristol glaze of fair luster, it has been found necessary to use 0.35–0.4 equivalent of ZnO; to have, for physical reasons largely, not more than 0.15 equivalent of raw clay and preferably not more than 0.1 equivalent; to keep the molecular ratio of SiO_2 : Al_2O_3 close to 5.5 or 6; and the equivalent of feldspar between 0.3 and 0.45, preferably at 0.4 equivalent.

Notwithstanding the considerable amount of research that has been devoted to the study of Bristol glaze combinations, we are still unable to give adequate reasons for the proportions that are peculiar to Bristol glazes. The researches along this line will be found in the Transactions of the American Ceramic Society, as follows: IV, 61; V, 136; IX, 483; XI, 618; XIII, 550. These articles seem to go as far in the obtaining of a fundamental understanding of this type of glaze as their methods of analysis permitted. It is now proposed to direct attention to a study of this type of glaze by what the petrographers call "Norms." See Staley, Trans. A. C. S., Vol. XIII, p. 126.

It is not necessary, at this time, to review the investigations which throw light upon this normative study of Bristol glazes, but a partial list of references is given:

1. H. O. Hoffman, Trans. Amer. Inst. Min. Engrs., Vol. XXIX, p. 682.
2. Boudouard, Jour. Iron and Steel Inst., 1905, p. 339.

[1] Contribution from the Ceramic Engineering Laboratory of the Ohio State University.

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3. Day and Shepherd, Amer. Jour. Sci., October, 1906.

4. Shepherd and Rankin, Jour. Ind. and Eng. Chem., Vol. III, No. 4, 1911.

5. R. Rieckie, Sprechsaal, Nos. 37, 38, 44, 45, 46, 1907.

6. Cross, Idding, Pirsson and Washington, "Quantitative Classification of Igneous Rocks," p. 146.

Shepherd and Rankin have summarized their observations on the CaO-Al_2O_3-SiO_2 mixtures in curves plotted on a triaxial diagram, the curves there shown being eutectic boundary lines, and the areas between the lines representing those mixtures of CaO-Al_2O_3-SiO_2 out of which the compounds indicated would be the first to crystallize. If made in relief, these eutectic lines would be valleys coursing in among small hills, as shown in elevation on melting-point curves (see Fig. 1).

Attention is directed to only two of the eutectic points on the Shepherd and Rankin triaxial diagram, those indicated by the numerals 2 and 5. The chemical composition and "Norm" constitution of these eutectic points are as follows:

Chemical composition			Norm constitution		
Eutectic No.	2	5	Eutectic No.	2	5
SiO_2	62.5	42	Anorthite	1	1
Al_2O_3	16.0	19	$2CaO\ Al_2O_3\ SiO_2$	..	1
CaO	21.5	39	Wollastonite	1.45	4.45
			Quartz	3.12	..

It has been supposed that Seger[2] had found the most fusible mixture of whiting, feldspar, clay and flint, and used the same as cone 4. It should be profitable, therefore, to dissect the cone 4 mixture into what would be its normative constitution if complete fusion should be obtained.

Since Seger found that no mixture of whiting and feldspar was more easily deformed as a cone than was the feldspar alone, and that the calcium made mixtures more fusible only when clay was present, we must assume that the feldspar was not effected to any appreciable extent chemically[3] and that it merely

[2] Seger's Collected Writings, Trans. A. C. S., p. 232.

[3] See melting-point curve for feldspar-whiting mixtures by Bleininger and Moore. Trans. A. C. S., Vol. X, page 263. This curve indicates that with 3 per cent. whiting and 97 per cent. feldspar there is a reaction giving a eutectic. The nature of this reaction is not revealed in this curve.

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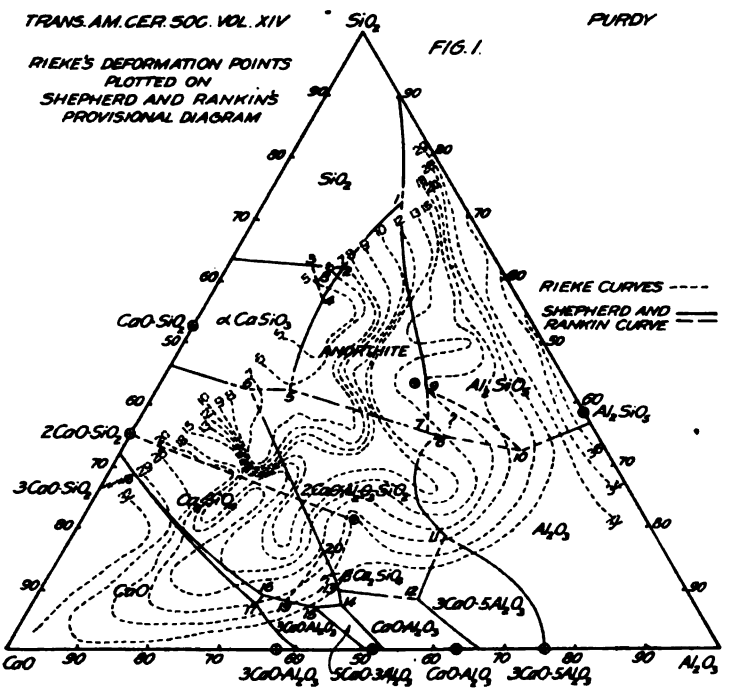

served as a component with the calcium compounds and with quartz to form the eutectic which was more easily deformed than feldspar alone. Indeed this assumption is fully in accord with petrographic findings.

As will be seen later in this text, there is no reason to believe that feldspar is effected chemically, even in completely fused Bristol glaze mixtures unless there is not sufficient silica present to satisfy the calcium and zinc oxides, and further, that if the feldspar should be so effected, it would be converted into leucite ($K_2O\ Al_2O_3\ 4SiO_2$), the pyro-properties of which are so like those of the orthoclase feldspar as to make but little difference in the behavior of the resultant fusion.

Calculation of the normative[4] constitution of completely

[4] While in the consideration of the normative constitution of Bristol glazes we have used definite mineralogical names, it should not be inferred that we believe these minerals are formed to any great extent in these glazes. What we believe is that should these glaze mixtures be carried to complete fusion, *i. e.*, the reactions all be completed, these mineral norms would be formed.

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fused cone 4 and of completely fused typical Bristol glaze mixtures makes it evident that the whiting, clay and flint of the Bristol glaze and of cone 4 would form compounds represented by points close to the eutectic line 2–5, that for cone 4 being just above and to the left of eutectic 2, and that for the Bristol glaze being nearer to eutectic point 5. It is in this latter region that we find, by Riekie's data and by iron furnace practice, the most fusible of these mixtures.

METHOD OF CALCULATION.

A. Taking as our glaze the following:

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.3\ CaO \\ 0.4\ ZnO \end{matrix}\right\}\ 0.4\ Al_2O_3\ 2.2\ SiO_2$$

we feel quite sure that the feldspar ($K_2O\ Al_2O_3\ 6SiO_2$) would be unaffected and that the silica would normally combine with calcium oxide much more readily than with the zinc oxide, thus forcing the zinc to be satisfied with the ortho silicate combination, $(ZnO)_2\ SiO_2$, as in willemite; hence, proceeding as in the usual glaze calculation, we have:

	K_2O	CaO	ZnO	Al_2O_3	SiO_2
	0.3	0.3	0.4	0.4	2.2
0.3 equivalent feldspar	0.3	...	...	0.3	1.8
	0.3	0.3	0.4	0.1	0.4
0.2 equivalent willemite	...	...	0.4	...	0.2
	...	0.3	...	0.1	0.2
0.1 equivalent $2CaO\ Al_2O_3\ SiO_2$	...	0.2	...	0.1	0.1
0.1 equivalent wollastonite	...	0.1	...	...	0.1

The normative constitution of this glaze, if carried to complete fusion, would therefore be:

0.3 equivalent orthoclase
0.2 equivalent willemite
0.1 equivalent $2CaO\ Al_2O_3\ SiO_2$
0.1 equivalent wollastonite.

B. To illustrate another method of attack, suppose we desire to formulate a glaze, the reactions within which would tend to form the minerals of eutectic 5, willemite, and orthoclase feldspar.

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0.05 equivalent anorthite
0.05 equivalent $2CaO\ Al_2O_3\ SiO_2$ } eutectic 5
0.223 equivalent wollastonite
0.2 equivalent willemite
0.227 equivalent orthoclase feldspar

The composite molecular formula of such a mixture would be:

0.373 CaO
0.400 ZnO } $0.328\ Al_2O_3\ 1.94\ SiO_2$.
0.227 K_2O

By varying the proportion of eutectic 5 and feldspar, we could obtain a mixture having a formula of:

0.1975 CaO
0.4000 ZnO } $0.456\ Al_2O_3\ 2.813\ SiO_2$.
0.4025 K_2O

Either of these mixtures could be used as Bristol glazes.

The noteworthy results of the foregoing analysis is the finding that in the glazes of the cone 4 type, the calcium compounds which, with complete fusion, would normally be formed are those of the eutectic 2 on the Shepherd and Rankin diagram, while in glazes of the Bristol type, the calcium compounds which would be involved are those in the neighborhood of eutectic 5.

Aside from the obvious inference that because the eutectic mixture 5 is much more fluid when fused, or at least has a much lower deformation point than the mixtures 2 and 4 (as shown by the plotting of Riekie's data on the Shepherd and Rankin diagram) and hence should, with a given heat treatment, develop greater maturity and gloss with a given proportion of orthoclase feldspar and willemite, we are still quite far from solving the questions concerning the cause for the several properties which are peculiar to this type of glaze. There still remains also the perplexing question concerning the narrow limits of variation in composition of glossy opaque cone 5–8 Bristol glazes.

THE INVESTIGATION.

It has often been proven that this type of glaze requires from 0.3 to 0.4 equivalent of feldspar. It is equally well established that unless the Al_2O_3 is relatively high, good opacity can not be obtained with much less than 0.4 equivalent of ZnO. We have, therefore, planned two series of mixtures (A and B)

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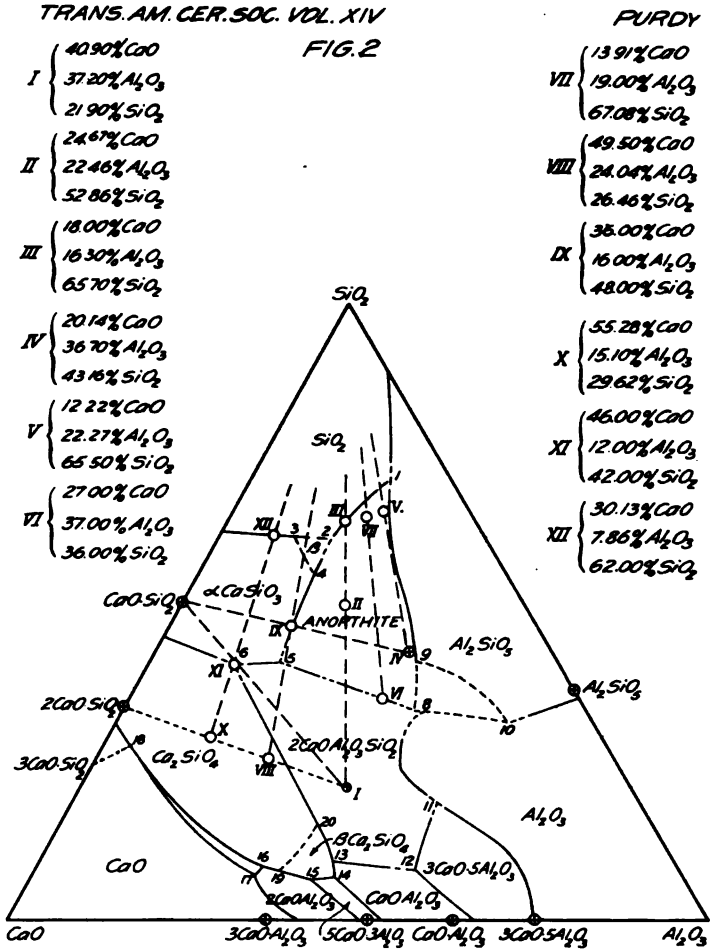
containing respectively 0.3 and 0.4 equivalent of feldspar, each glaze to contain 0.2 equivalent of willemite and the principal variations in the several glazes to be between the calcium compounds and in some cases free silica as shown on Fig. 2.



SHEPHERD-RANKIN PROVISIONAL DIAGRAM ON WHICH IS SHOWN THE NORMS USED IN MAKING THE BRISTOL GLAZES.

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I. The composite molecular formula of A 1 would be made up as follows:

	ZnO	K_2O	CaO	Al_2O_3	SiO_2
0.2 equivalent willemite.....	0.4	...	...	..	0.2
0.15 equivalent $2CaO\ Al_2O_3\ SiO_2$.....	...	...	0.3	0.15	0.15
0.3 equivalent orthoclase.....	...	0.3	...	0.3	1.8
	0.4	0.3	0.3	0.45	2.15

In the same way the composite molecular formula of B 1 is found to be:

B 1

$$\left.\begin{matrix} 0.4\ ZnO \\ 0.4\ K_2O \\ 0.2\ CaO \end{matrix}\right\} 0.5\ Al_2O_3\ 2.7\ SiO_2$$

II. The location of Glazes 2 was chosen because it represents the minerals which, with orthoclase and willemite, would normatively result from the addition of only 0.3 molecule SiO_2 to the mixture for B 1. The normative constitution of this mixture would be:

0.4 equivalent orthoclase ($K_2O\ Al_2O_3\ 6SiO_2$)
0.2 equivalent willemite ($2ZnO\ SiO_2$)
0.1 equivalent anorthite ($CaO\ Al_2O_3\ 2SiO_2$)
0.1 equivalent wollastonite ($CaO\ SiO_2$)
0.1 equivalent silica (SiO_2)

The composite molecular formula of this Glaze 2 in the A series (with 0.3 equivalent orthoclase) is:

A 2

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.4\ ZnO \\ 0.3\ CaO \end{matrix}\right\} 0.45\ Al_2O_3\ 2.4\ SiO_2$$

III. By further increasing of the SiO_2 in Glaze 1, we may obtain one that would be represented by point 3 on the diagram.

A 3

$$\left.\begin{matrix} 0.3\ K_2O \\ 0.4\ ZnO \\ 0.3\ CaO \end{matrix}\right\} 0.45\ Al_2O_3\ 2.82\ SiO_2$$

B 3

$$\left.\begin{matrix} 0.4\ K_2O \\ 0.4\ ZnO \\ 0.2\ CaO \end{matrix}\right\} 0.5\ Al_2O_3\ 3.42\ SiO_2$$

IV. Glazes 4 would be a mixture of anorthite, orthoclase and willemite and have the following composite molecular formulae:

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A 4		B 4	
0.3 K_2O 0.4 ZnO 0.3 CaO	0.6 Al_2O_3 2.6 SiO_2	0.4 K_2O 0.4 ZnO 0.2 CaO	0.6 Al_2O_3 3.0 SiO_2

V. By increasing the SiO_2 in Glazes 4, we obtain the following composite molecular formulae without any change in the Norms other than in the proportion of free silica.

A 5		B 5	
0.3 K_2O 0.4 ZnO 0.3 CaO	0.6 Al_2O_3 3.2 SiO_2	0.4 K_2O 0.4 ZnO 0.3 CaO	0.6 Al_2O_3 3.6 SiO_2

VI. By using the eutectic between anorthite and 2CaO Al_2O_3 SiO_2 (0.24 and 0.12 equivalent, respectively), we obtain the composite molecular formulae for Glazes 6.

A 6		B 6	
0.3 K_2O 0.4 ZnO 0.3 CaO	0.525 Al_2O_3 2.375 SiO_2	0.4 K_2O 0.4 ZnO 0.2 CaO	0.55 Al_2O_3 0.85 SiO_2

VII. Adding silica to these glazes in order to bring the SiO_2/Al_2O_3 ratio closer to that which is usually used, we arbitrarily adopt the following composite molecular formulae for Glazes 7:

A 7		B 7	
0.3 K_2O 0.4 ZnO 0.3 CaO	0.525 Al_2O_3 2.825 SiO_2	0.4 K_2O 0.4 ZnO 0.2 CaO	0.55 Al_2O_3 3.3 SiO_2

This addition of 0.65 molecule of SiO_2 to Glazes 6 so changed the Norms that in place of the eutectic between anorthite and 2CaO Al_2O_3 SiO_2, we have 0.15 equiv. of anorthite, 0.05 equiv. of wollastonite, and 0.35 equiv. of free silica.

VIII. For Glazes 8 we have chosen a point on the line connecting the points for the compounds 2CaO SiO_2 and 2CaO Al_2O_3 SiO_2 such that, by mere increase of SiO_2 in the composite molecular formulae, we may secure the eutectic between anorthite and wollastonite which we aim to use in Glazes 9.

The composite molecular and normative formula of A 8 and B 8 are as follows:

	A 8
0.3 K_2O 0.4 ZnO 0.3 CaO — 0.38 Al_2O_3 2.15 SiO_2	0.3 equivalent orthoclase 0.2 equivalent willemite 0.08 equivalent 2CaO Al_2O_3 SiO_2 0.07 equivalent 2CaO SiO_2

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B 8

$0.4\ K_2O$, $0.4\ ZnO$, $0.2\ CaO$ } $0.453\ Al_2O_3\ 2.7\ SiO_2$

0.4 equivalent orthoclase
0.2 equivalent willemite
0.0534 equivalent $2CaO\ Al_2O_3\ SiO_2$
0.0466 equivalent $2CaO\ SiO_2$

IX. By calculations from Shepherd and Rankin's diagram, we find the eutectic between anorthite and wollastonite to be 0.166 equiv. $CaO\ Al_2O_3\ 2SiO_2$, 0.459 equiv. $CaO\ SiO_2$.

Glazes 9, therefore, have the following composite molecular formulae:

A 9

$0.3\ K_2O$, $0.4\ ZnO$, $0.3\ CaO$ } $0.38\ Al_2O_3\ 0.38\ SiO_2$

B 9

$0.4\ K_2O$, $0.4\ ZnO$, $0.2\ CaO$ } $0.453\ Al_2O_3\ 2.853\ SiO_2$

X. By so locating Glazes 10 on the line drawn between composition points for the compounds $2CaO\ Al_2O_3\ SiO_2$ and $2CaO\ SiO_2$, such that by mere increase in SiO_2 in the composite molecular formula we may have the next glazes (11) with Shepherd and Rankin's eutectic 6, we find that the composite molecular formula and equivalent norm constitution of Glazes 10 will be as follows:

A 10

$0.3\ K_2O$, $0.4\ ZnO$, $0.3\ CaO$ } $0.345\ Al_2O_3\ 2.15\ SiO_2$

0.3 equivalent orthoclase
0.2 equivalent willemite
0.105 equivalent $2CaO\ SiO_2$
0.045 equivalent $2CaO\ Al_2O_3\ SiO_2$

B 10

$0.4\ K_2O$, $0.4\ ZnO$, $0.2\ CaO$ } $0.43\ Al_2O_3\ 2.7\ SiO_2$

0.4 equivalent orthoclase
0.2 equivalent willemite
0.07 equivalent $2CaO\ SiO_2$
0.03 equivalent $2CaO\ Al_2O_3\ SiO_2$

XI. Shepherd and Rankin's eutectic 6 consists of:

0.579 equivalent $CaO\ SiO_2$
0.0034 equivalent $2CaO\ SiO_2$
0.1176 equivalent $2CaO\ Al_2O_3\ SiO_2$

The use of this eutectic in Glazes 11 of our series results in the following composite molecular formulae:

A 11

$0.3\ K_2O$, $0.4\ ZnO$, $0.3\ CaO$ } $0.343\ Al_2O_3\ 2.26\ SiO_2$

B 11

$0.4\ K_2O$, $0.4\ ZnO$, $0.2\ CaO$ } $0.429\ Al_2O_3\ 2.77\ SiO_2$

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XII. By a further increase of SiO_2 in the composite molecular of Glazes 10, we obtain those of 12. The point 12 represents a mixture of

0.077 equivalent anorthite
0.461 equivalent wollastonite
0.418 equivalent silica

When figured into our series, we have:

A 12

0.3 K_2O
0.4 ZnO
0.3 CaO
} 0.343 Al_2O_3 2.575 SiO_2

B 12

0.4 K_2O
0.4 ZnO
0.2 CaO
} 0.429 Al_2O_3 2.98 SiO_2.

Collecting the Al_2O_3 and SiO_2 of these composite molecular formulae, we have:

Series A			Series B		
RO 0.3 K_2O 0.4 ZnO 0.3 CaO	Al_2O_3	SiO_2	RO 0.4 K_2O 0.4 ZnO 0.2 CaO	Al_2O_3	SiO_2
A 1.....	0.45	2.15	B 1..	0.5	2.7
A 2.....	0.45	2.4	B 2..	0.5	3.0
A 3.....	0.45	2.82	B 3..	0.5	3.42
A 4.....	0.60	2.6	B 4..	0.6	3.0
A 5.....	0.60	3.2	B 5..	0.6	3.6
A 6.....	0.525	2.375	B 6..	0.55	2.85
A 7.....	0.525	2.825	B 7..	0.55	3.3
A 8.....	0.38	2.15	B 8..	0.453	2.7
A 9.....	0.38	2.38	B 9..	0.453	2.85
A 10.....	0.345	2.15	B 10..	0.43	2.70
A 11.....	0.343	2.26	B 11..	0.43	2.77
A 12.....	0.343	2.575	B 12..	0.43	2.98

These glazes were burned to cone 6 in 20 hours.

DISCUSSION OF RESULTS.

Opacity.

Observations.—Of these glazes, 4, 5, 6 and 7 of both series are the whitest, *i. e.*, they are the most opaque. Of these four glazes, the most opaque are 4 and 6.

Glazes 1, 2, 3 and 8, both series, rank next to the above group of glazes in order of opacity.

Glazes 9, 10, 11 and 12, both series, are transparent.

Conclusions.—(1) With 0.3 to 0.4 equiv. orthoclase and

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0.2 equiv. willemite, maximum opacity is obtained when anorthite is the only other mineral that would normatively be formed.

(2) Next to anorthite, we find that 2 CaO Al_2O_3 SiO_2 is the best supporter of opacity.

(3) As the content of either 2 CaO SiO_2 or CaO SiO_2 increases in amount, the opacity is decreased, the CaO SiO_2 being the more powerful in destruction of opacity.

(4) While increase of SiO_2 in any of these mixtures decreases opacity to some extent, the trials show that the opacity is but very slightly affected when increase in SiO_2 does not result in formation of wollastonite, and that in those cases in which the increase of SiO_2 causes the formation of wollastonite, there is a decided decrease in opacity, the decrease being directly proportional to the increase in wollastonite.

(5) While the present series do not show the effect of increased heat treatment, we know from many other experiments that opacity is thus decreased, but that the effect of increased heat treatment is much less pronounced in those glazes high in anorthite and is scarcely perceptible when sillimanite (Al_2O_3 SiO_2) is present.

(6) The use of eutectic mixtures, such as, for illustration, that between anorthite and wollastonite and that between anorthite and 2 CaO Al_2O_3 SiO_2, is apparently without effect on opacity. The support of opacity seems to be an additive function of the mineral norms produced in the glaze. We found this to be the case without exception in a normative study of the glazes reported in Volumes V and XIII.

(7) It is impossible to decide why anorthite is a better supporter of opacity than wollastonite and the metasilicate, 2 CaO SiO_2. It is obvious that this difference is not due to differences in fusibility of these minerals for their melting points are as follows:[5]

Wollastonite	1540° C.
2CaO SiO_2	2130° C.
Anorthite	1552° C.

One plausible conjecture is that the anorthite-orthoclase mixture, while possibly not less fusible, is a poorer solvent for

[5] Amer. Jour. Sci., Vol. XXXI, May, 1911, p. 346.

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the willemite than is either the ortho- or meta-calcium silicate-orthoclase mixture. Length of time of heat treatment may here be very effective for it is known that the calcium silicates are formed much more readily, that is, the reactions resulting in their formation are much more rapid than in the case of anorthite.

In support of this latter theory, we have the actual laboratory and factory experience that the greater the time of heat treatment, the less opaque will be the glaze. In matte glazes also, we have very strong evidence that the matte texture is due to the holding in suspension of materials that are either combined or will combine to form anorthite, and the heat range in which the glaze will remain as a matte depends upon the rate of formation and solution of the anorthite.

That maintenance of opacity may be due, in part, to both of these causes, *i. e.*, difference in solvent action of the magma and in rate of formation of the calcium compounds, is shown by the fact that while opacity in the anorthite Bristol glaze mixtures is decreased some by increased heat treatment, even cone 12 is not sufficient heat treatment to destroy the opacity to a very large extent.

(8) Our theories concerning the cause and maintenance of opacity in these glazes are not unlike those stated on pages 571–577, Vol. XIII of our Transactions, except that now we believe we understand more clearly why the varying factors there described have the effect which they were said to have.

(9) The presence of sillimanite, of course, adds to the opacity and at the same time makes the glazes very much more refractory. Sillimanite is not necessary to the development of good opacity when we have 0.2 equiv. of willemite present. The beneficial effect of increase in the Al_2O_3, shown in the composite molecular formulae, is not caused by the Al_2O_3 itself but by a change in calcium compounds from wollastonite to anorthite.

(10) Variation in the equivalent of feldspar required to make up the glaze batch has very little effect on the opacity, simply because as the feldspar increases the equivalent of whiting and clay decreases, the net effect being a substitution of orthoclase for anorthite, or *vice versa*. Such a substitution does not seem

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to appreciably effect the development or maintenance of opacity.

(11) Opacity is due to willemite (2 ZnO SiO_2) held in suspension, *i. e.*, not completely taken into solution. The presence of the anorthite or orthoclase and the absence of the calcium silicates aid indirectly in the development of opacity by their effect upon the rate and extent of solution of the willemite. It is plainly a case of supersaturation under the time-temperature conditions of the fusion, rather one of a compound separating out.[6]

Gloss.

(1) Glaze 4, Series B (containing 0.4 equiv. of feldspar), has more gloss than has Glaze 4, Series A (0.3 equiv. feldspar), but neither has much gloss. Glaze 4, Series A, is almost a matte.

(2) The best gloss was obtained in the glazes having the highest content of wollastonite (CaO SiO_2), the gloss varying directly with wollastonite content.

All the mixtures were more glossy than the anorthite mix (Glaze 4), but next to the effect of wollastonite, the most noticeable one was that of increase of SiO_2. This effect of increase in SiO_2 is to be seen in the increased gloss from Glaze 4 to Glaze 5.

(3) The development of gloss in these incompletely fused glazes seems to be due to two factors—surface tension and degree of fusion. This we have discussed before.[7] This was clearly shown in a normative study which the Class of 1912 made of the glazes described in Vol. XIII. The general conclusion was that the most glossy glazes were those which, when plotted on Shepherd and Rankin's provisional diagram, were nearest to the wollastonite area and that of these high wollastonite mixtures, those having the largest content of willemite (2 ZnO SiO_2) were the most glossy.

(4) Increase of feldspar has but slight effect on the gloss of these glazes for with each increase in feldspar content, if the total Al_2O_3 equivalent is kept constant, there is an increase in the proportion of wollastonite to the total sum of the feldspars

[6] Compare with Parmelee, Vol. IX, Trans. A. C. S., page 597.
[7] See Trans. A. C. S., Vol. XIII, page 583.

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(orthoclase, anorthite and leucite). This is shown by the following proportions found in Glaze 1, Series C, of each of the five groups of glazes described in Vol. XII of the Transactions.

	Groups				
	1	2	3	4	5
Equivalent feldspar	0.2	0.25	0.333	0.40	0.50
Ratio of wollastonite to the feldspars by molecules	5.9	8.3	14.3	23.2	28.6
	29.4	33.4	42.8	55.5	57.6
Amount in molecules per unit of the feldspar	0.2	0.248	0.336	0.42	0.5

(5) To obtain *opaque* glazes which have sufficient gloss to satisfy commercial demands, one should choose such mixtures as those of VI C and VI D of the Bristol glaze series described in Vol. V of the Transactions. The normative constitutions in equivalents of these glazes are:

	VI C	VI D
Orthoclase	0.4	0.4
Anorthite	0.12	0.16
Wollastonite	0.08	0.04
Willemite	0.20	0.20
Silica	..	0.12

These mixtures, it should be noted, lie almost on the same line as Glazes 6 and 7 of the present series. These contain enough wollastonite to have good gloss, and yet not enough to greatly decrease the opacity or to cause physical defects.

Physical Defects.

Under this head we will consider only two defects, crawling and crazing.

Crawling.—(1) Crawling was very pronounced in Glazes 8, 9, 10, 11 and 12; that is, in those glazes in which wollastonite was present in largest amounts. Of these five glazes, 11 and 12 crawled the worst.

(2) Glaze 4, containing anorthite ($CaO\ Al_2O_3\ 2\ SiO_2$), did

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not crawl while Glazes 1 and 6, containing 2 CaO Al_2O_3 SiO_2, crawled slightly.

(3) Increase in SiO_2 increased the tendency to crawling even in Glaze 5, which contained no wollastonite.

(4) The glazes of Series B (0.4 equiv. feldspar) have crawled worse than those of Series A (0.3 equiv. feldspar).

Crazing.—(1) The glazes of Series A (0.3 equiv. feldspar) which show crazing are Nos. 8, 9, 10 and 11.

(2) The glazes of Series B (0.4 equiv. feldspar) which show crazing are Nos. 1, 6, 8, 9, 10, 11 and 12.

(3) It is evident from these observations (they check previous findings) that crazing follows from increase either in orthoclase feldspar or in wollastonite and that crazing decreases with increase in either anorthite or silica.

(4) It is noticed that wherever there is a tendency to crawl, there we have crazing, and that crazing is the worst in those glazes that have crawled the most.

(5) Crazing is due to shrinkage in volume and to surface tension. Strains certainly must arise from this drawing up of the glaze and these can find relief only in the cracking of the glaze. The shrinkage in volume of the mass due to changes in mineral constitution and the volume changes which these newly formed minerals pass through when cooling after having attained rigidity, we consider as being sufficient to account for all the strains necessary to produce crazing. We need not resort to the untenable supposition o there being differences in coefficient of expansion and contraction between the body and glaze to account for these glaze defects.

In conclusion, I wish to credit Professor Homer F. Staley for the inspiration which I received from reading his discussion on Norms,[8] and which prompted this present research.

While such an analysis of the partially fused Bristol glaze mixtures must be hypothetical, it gives us definite pictorial understanding of the effects of changes in the formulae of glazes which can not be obtained from the usual composite molecular formula. This method of study is not new for many have con-

[8] Trans. A. C. S., Vol. XXIII. pp. 126–131.

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jectured in the same way, but with less definite data, concerning the constitution of glasses, slags and cements.

DISCUSSION.

Prof. Bleininger: I would like to ask whether all of this work is based on Geophysical Laboratory data.

Mr. Purdy: The Geophysical Laboratory has, for some time, been studying the compounds that would be formed in fusion and has issued this preliminary diagram of the calcium-alumina-silica compounds

Petrographers have been studying the composition of rocks for some time, and they are the ones who originated this normative study of igneous solution. They have made thousands of such studies, and so far as I know the only criticism that has grown out of these studies concerns the attempt to classify rocks from "Norm" calculations rather than from the "Modes."

Prof. Bleininger: I do not agree with Mr. Purdy when he says these attempts have been successful. I understand Mr. Purdy's aim, I think, and I think he deserves credit for applying this idea to ceramic problems. However, I do not think we are justified at the present time in making such assumptions at all. A good many of the facts which are brought out by Mr. Purdy may be explained by any similar compound, whatever you name it. He may say a silicate of the type of wollastonite will act in such a manner. Why not say then that we are dealing with silicates of the RO SiO_2 or the RO 2 SiO_2 types?

Mr. Purdy: You consider this work worthless?

Prof. Bleininger: No serious work is worthless, but I am afraid that Mr. Purdy has gone a little too far with the data at hand. In several years at the rate at which they are working, it may be possible to do something like this.

Mr. Purdy: Mr. Chairman, I distinctly state that this method of study is based on hypothesis rather than observations. This is shown by the use of the term "normative." A normative study of rocks is a sort of prophecy of what minerals the fused mass would crystallize into if given an opportunity. Actual data shows that while such a prophecy can not be made with

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accuracy in rock magmas, the calculated prophecy and observed facts do coincide remarkably close.[9]

Prof. Bleininger: I still object to the use of terms implying the formation of definite minerals.

Mr. Purdy: What assumption have I made?

Prof. Bleininger: As to the formation of these silicates.

Mr. Purdy: We do not make such assumptions. We assume that if conditions permitted, these minerals would be formed. We find justification for this in the thousands of calculations that Cross, Idding and Washington have made. We find further justification for this in the fact that when CaO Al_2O_3 and SiO_2 are properly proportioned and mixed by fusion,

[9] "Under 'Norm' is given the composition in standard or conventional minerals and under 'Mode' the percentage of the species actually present in the rock.

Composition of Butte Granite

Norm			Mode		
Quartz		19.38	Quartz		22.86
Orthoclase	25.02	66.67	Orthoclase	18.35	58.09
Albite	23.58		Albite	23.06	
Anorthite	18.07		Anorthite	16.68	
Diopside	0.67	7.45	Biotite	10.92	14.48
Hypersthene	6.78		Hornblende	3.56	
Magnetite	3.01	4.23	Magnetite	1.86	2.32
Ilmenite	1.22		Ilmenite	0.46	
Pyrite	0.24	0.55	Pyrite	0.24	0.55
Apatite	0.31		Apatite	0.31	
Etc		0.99	Etc		0.85
		99.27			99.15

"The divergence between convention and reality is evident at a glance. In many cases, however, the norm and mode of a rock are practically identical, and then the standard computation is more satisfactory. The normative and actual minerals may or may not be the same. Some discrepancies, however, exist, to which much weight can not be given. In calculating the percentage of a mineral from the proportions of oxides shown by analysis, there is a strong tendency toward the multiplication of errors. Alumina, for instance, is often uncertain, at least in ordinary analyses of fair average quality, by as much as one-half of 1 per cent. This amount corresponds to an error in orthoclase, if all the alumina goes to that mineral, of 2.7 per cent., and the variation entrains others, especially in the estimation of the residual quartz. The computed mineral composition of a rock is correct by multiples of the errors existing in the analysis, and these may be, in fact are, sometimes large.

"The normative or standard minerals, then, so far as the make-up of a rock is concerned, are partly real and partly conventional. They are, however, quantitative in application and give uniformity to the discussion of rocks. Upon them the quantitative classification is founded."—F. W. Clarke, "The Data of Geo Chemistry," Bull. 496, page 406, U. S. G. S.

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you can obtain anorthite, etc., etc. I concede that whether or not these compounds were formed in the glaze is immaterial. We do not make the assumption that they are formed. We know that anorthite will be formed if we have the norm and sufficient fusion. Feldspar will not be seriously affected unless there is not sufficient silica to satisfy the other bases. As to the zinc silicate being formed, we do not know that.

Prof. Bleininger: I simply object to calling the theoretical silicates minerals. I am not objecting at all to the procedure, as a whole, since it has been applied by Jueptner to slags, Zulkowski to glasses, and by others to cement.

Mr. Potts: Professor Bleininger objects to Mr. Purdy's use of the names of definite minerals in his discussion but he loses sight of the manner in which the writer of the paper uses the terms. The argument is expressly stated in the following manner: "If the oxides are present in the proportions to form wollastonite, anorthite, etc." Naturally as the paper proceeds this form of expression is changed but for convenience only, the sense is still retained.

Mr. Purdy: I am aware of the importance of the suggestion Professor Bleininger is making but I still feel warranted in speaking of these "norms" in terms of definite minerals. This is not a new procedure and one need not go beyond our own Transactions for examples. Professor Stull has given in Volume VI, page 186, an excellent paper on crystalline glazes that contains much that may be said to be of the same sort as our normative study. In this paper he shows the futility of attempting to mix minerals in the expectation of thus producing a glaze, but his attempts in this shows very nicely the value of using our knowledge of minerals in the study of glazes.

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DOWNDRAFT KILN BOTTOMS.

By T. W. GARVE, Columbus, O.

Most of the kiln bottoms incorporated in this paper are taken from the files of The Richardson-Lovejoy Engineering Co.; some are of recent date, but all have demonstrated in actual operation their practicability and efficiency under conditions for which they were designed. We have included several kiln bottoms of other designers and have given them credit; but we have made no attempt to fully cover the field, which would be a task of exceeding magnitude.

The full page drawings of these bottoms are not intended to represent working drawings, for such would not allow an easy comparison of the various types and would be out of place here. In arranging different sections on different sides of the main center lines, it was possible to make each case perfectly clear without going into elaborate drafting work and detailing. For the simpler types of the bottoms or for modifications, only one section or view is given without any sacrifice on the point of clearness. The sections are taken so that each drawing brings out plainly the characteristics and peculiarities of each bottom, and with these drawings before us, it will be convenient to study the different designs.

When we glance over these bottoms, it appears as if they were unduly complicated. It must be borne in mind, however, that the bottom of a downdraft kiln, as its most essential part, has to serve three important purposes: first, it must accomplish a uniform heat distribution all over the kiln; second, it must act as a damper to check the flow of gases, thus giving time for the absorption of the heat by the ware; third, it must act as a heat conserver, that is, it must take up as many heat units as possible from the gases after they have performed their main duty in the kiln so that the ware on the floor, receiving only the last benefit from the down-going gases, may profit by the radiation of heat stored within the lower brick work. Further, in regard to the first mentioned purpose, an equal distribution of heat does not necessarily mean an equal pull on all the openings distributed over the floor. The kind of ware, the manner of

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setting, and the tendency or natural flow of the gases must be taken into consideration. If the floor openings are so distributed as to fit themselves to these requirements, then, undoubtedly, there prevails an equal pull from below on all of the floor openings. In most cases, however, when we are dealing with all perforated or regularly perforated floors, the strongest draft should always be maintained at such spots or places as by reason of ware, setting, or flow, will either be neglected or will not receive the necessary overdraft in comparison with the rest. And, finally, after the gases have reached the lower flue system, they should find the same resistance until they unite in the main draft flue or stack.

On the upper part of the bottom, dirt pockets should be provided where the dirt can lodge and can easily be taken out occasionally, the removal preventing its accumulation in the lower flue system. These points will be brought out more clearly in the discussion of the various types of bottoms.

Only with perfect knowledge of these conditions and knowledge of the prevailing local conditions can a proper kiln bottom be designed or recommended. Some experimenting or final adjustments may become necessary in some cases; but these chances should have been reduced to an unavoidable minimum beforehand by careful consideration and study, since they are costly and often troublesome.

ROUND KILNS.

In Fig. 1 we have a representation of the center well type, and one having an all perforated floor. The gases, after their passage through the ware, enter the parallel under-floor flues through slots left between the floor bricks.

The gases will travel along these under-floor flues until they reach the nearest bottom openings. On the drawing, these bottom openings are brought out by dark shading, and there are three above each radial flue. Naturally the draft will be strongest above such an opening.

In order to equalize the draft, the under-draft flues are broken by cross walls and openings made through the feather walls into the adjacent draft flues, in order that each draft opening into the radial flues may control its own proper area of the floor.

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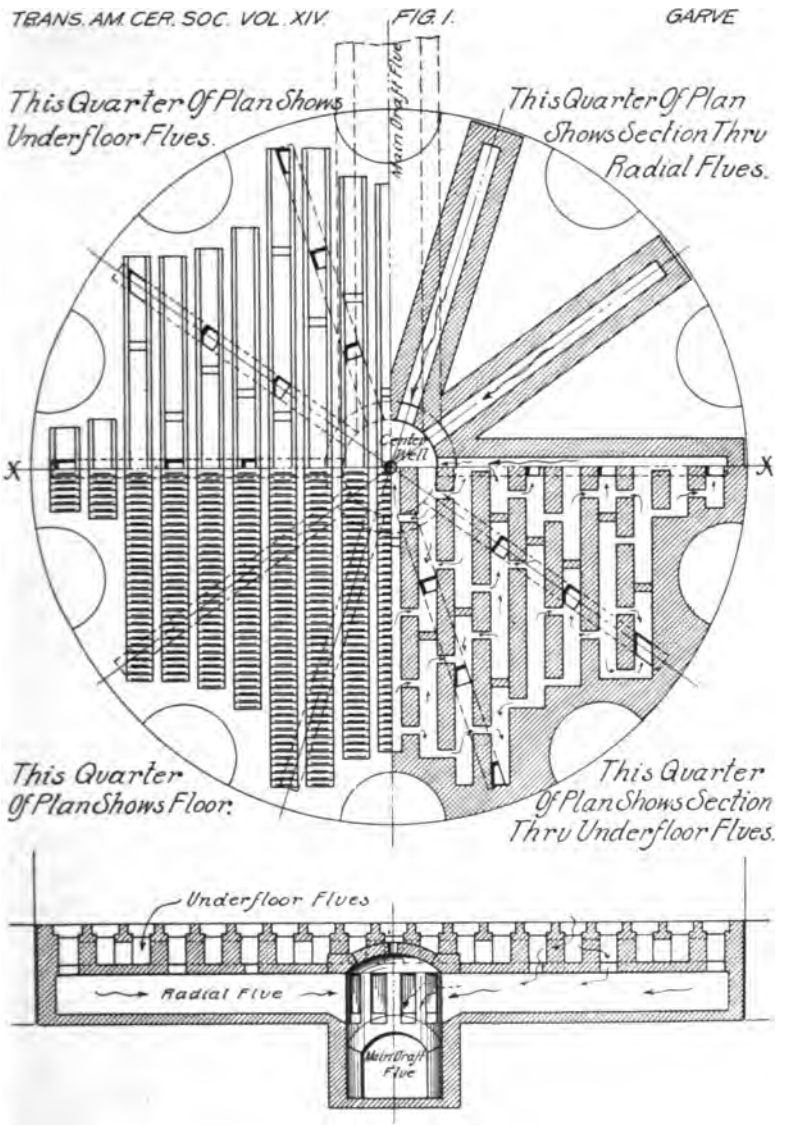

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It would involve but little trouble to make, if necessary, final adjustments in these cross walls or feather wall openings with loose bricks.

The cross walls would not be required for bottoms with alternating open and blind under-floor flues, as we shall see on the later drawings. It might be good practice not to use perforations immediately above the draft openings but instead to lay the floor brick tight here for the length of 12 to 18 inches, which would check the draft at those spots and prevent the sand and dirt from falling right through into the lower flues.

The radial flues start between the bags of the furnaces and carry the gases direct to the center well. The gases from all the radial flues overcome the resistance of one 90° turn in entering the center well, which insures an equal pull on all of them. This easily accomplished effect is a distinctive feature of the center well type The main draft flue should always be below the radial flues and not take the place of one of them.

A disadvantage of such a kiln bottom is its depth and in connection therewith a deep stack, provided the stack is close to the kiln. In one instance we had a total depth of about 8 feet, which was below ground-water level, as we learned later. In order to overcome the difficulty, we simply introduced a center stack without making any other changes in the design of the kiln bottom and thus reduced the total depth of 8 feet to less than 4 feet. This shows how close a relation there may be between a center well, outside stack, kiln and a center (inside) stack kiln. The same shallow bottom can be had if we use wall stacks, cutting out the center well entirely, but leaving the radial flues and putting a small wall stack at the outer end of each radial flue. Thus, Fig. 1 really illustrates three distinct types of kilns.

Another disadvantage of this bottom would be the weakness of the brick work on the upper center well where the radial flues enter. For large kilns or such as require high furnace power and hence have many radial flues, this weak point could be overcome by using a very large center well. If this is not desired, a ring flue near the center well can be introduced, and the center well be made only such size as is required to get entrance into the main draft flue. This ring flue would con-

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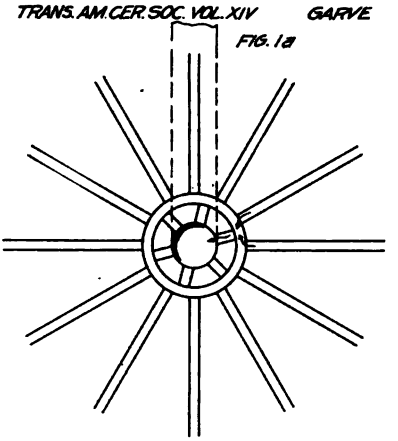
nect with the center well by short radial flues arranged between two of the long radial flues. This idea is shown in Fig. 1*a*.



An advantage of this type of bottoms (Fig. 1) is the possibility of laying the main draft flue at any angle desired without affecting the draft conditions or without affecting the layout of the upper floor in regard to the wickets, and hence its adaptability to the yard layout.

This bottom is well adaptable to kilns for burning sewer pipe. The floor is shown perforated throughout to warrant a good distribution of the salt vapors to all parts of the ware. The outer openings above the radial flues are comparatively large to give the desired strong pull between the bags at the floor, since the gases, after their overturning motion, will tend to catch the pipes nearest to the center of the kiln and pass down in these vertical pipe flues until they reach the floor.

Fig. 2 we have termed letter H bottom. Here, as well as in the next two or three bottoms, we have alternating blind and open under-floor flues. The open flues are covered by special floor bricks in the same manner as described for the previous kiln. The blind flues are covered tight by two courses of standard bricks or tiles, set in loose and with their joints broken. The gases, received in the open under-floor flues, will move along until they find the nearest opening in a feather wall to

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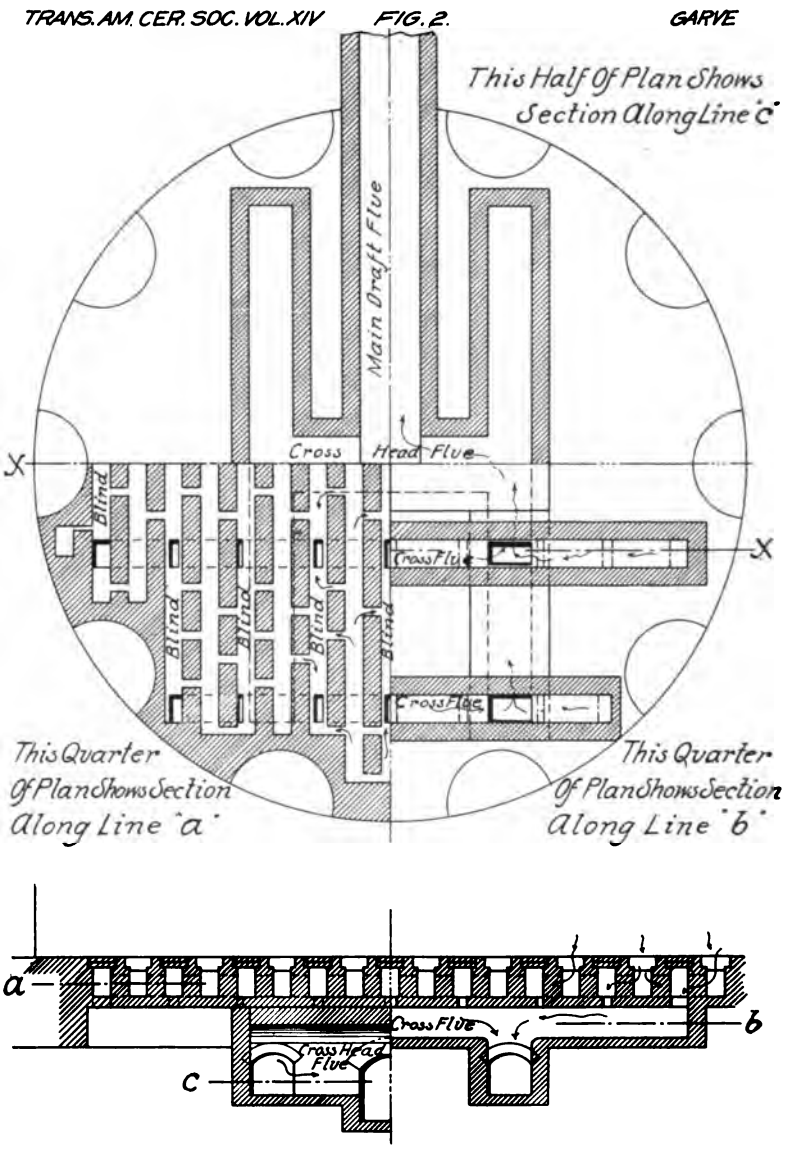

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enter the neighboring blind flue; thence they have to move along until they reach one of the bottom openings, shown on drawing dark shaded. The openings in the feather walls between the open and blind under-floor flues should not be too close to the bottom openings in the blind flues, and they should become longer or more numerous the farther away they are located from the said bottom openings in order to get good draft distribution and circulation of the gases.

It hardly needs to be mentioned again that here also, as in the previous case, final adjustments can be made by adding or removing loose brick to or from the feather wall openings.

Through the bottom openings of the blind flues, the gases enter the cross flues, of which there are four. Only the half length of two such cross flues show up in sectional plan taken along line "*b*." These cross flues have outlets from the bottom into the letter "H" flues, and it will be noticed that the openings in the top of the cross flues are smallest near these outlets and largest away from them. These outlets of the inner cross flues should be dimensioned accurately to take care of the amount of gases coming out of the top openings of these inner cross flues, since outlets excessively large here would allow too hard a pull from the kiln center.

The corresponding outlets of the outer cross flues, however, can be slightly larger without distributing the draft balance, provided the letter "H" flues are properly dimensioned. The gases from the four legs of the letter "H" flues are drawn toward the center, and before entering the cross head flue, they all have to make a turn of 90°. The cross head flue in its center is connected with the main draft flue.

From a constructive standpoint, this bottom has the advantage of having only rectangular flues and walls. This bottom as drawn has a depth of 7′ 6″ to the bottom of the main flue, but this can be reduced where conditions require to about 6′.

This bottom works especially well for the number and arrangement of furnaces shown, since the cross flues, though properly spaced, just get into the space between the bags and so can be carried out to the circumference of the bottom—but it does not always work so nicely.

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The dependence to some degree of this type of bottom upon the number of furnaces is one of its disadvantages. The location of all the flues in relation to each other is fixed and the direction of the main draft flue determines the direction of the under-floor flues; they all should be parallel as seen on the drawing. And since the location of the wickets in many cases is dependent upon the direction of the under-floor flues (open flues hence all under-floor flues), it will be understood that this type of bottom cannot claim the same elasticity in regard to the yard arrangement as the center well type; and in some situations this is another disadvantage. It must be mentioned, however, that this disadvantage is not prohibitive, since, first, the main draft flue can be curved or bent outside of the kiln bottom to reach its destination (the slight disadvantages of this curvative or bend being taken into consideration) and, second, the center line through the wickets could either be at a right angle or parallel to the under-floor flues for setting brick and at any angle whatsoever for any ware except bricks that are set in benches.

In Fig. 3, we have a modification of the bottom just described and, therefore, do not need to go again into a detailed explanation. With the introduction of an outer ring flue we have greater latitude in the number and arrangement of the furnaces. It will be noticed that the two short under-floor flues near each wicket are open to get a little stronger draft at the wickets, where otherwise the coldest spots would be.

In laying out such a bottom, it should be arranged that the four lower flues leading from the ring flue into the sides of the short cross head flue do not get too much of an angle with the main center line of the main draft flue and that their inlets are not too close to the entrance of the main draft flue. Failure to observe the last precaution would give an advantage to the gases coming from the flues opposite the main draft flue entrance, while the gases from the two opposite flues would have to overcome more friction in a complete turn.

In regard to the disadvantages of this type, the same will hold here that has been said about the previous bottom, and this was of only little consequence. For the disadvantage of

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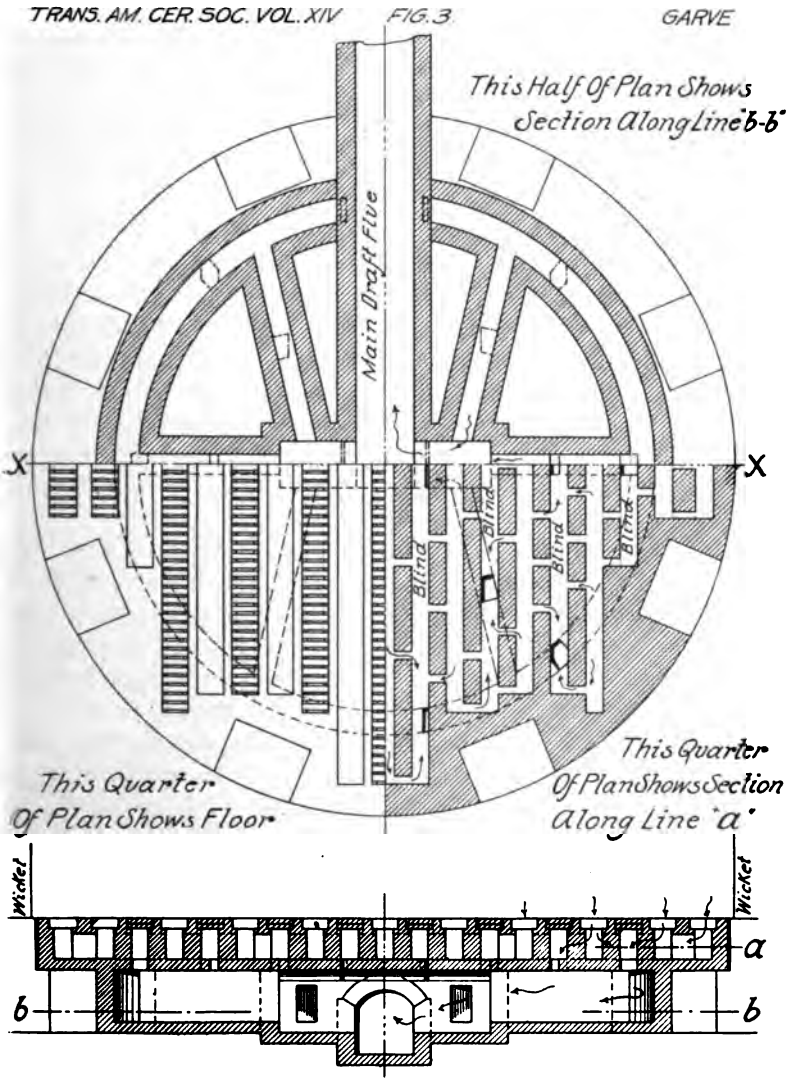

Section X-X

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constructing a circular flue (which is of little moment), we have a noted advantage of this type over the previous one in so far as only one set of flues is placed above another while the previous bottom really has three sets of flues built one above another. Therefore another advantage of this bottom is little depth.

Special attention may be called to the next bottom (Fig. 4), which is distinguished by simplicity. There are only under-floor flues, one cross head flue, and the main draft flue. Here it is quite essential that the feather walls have the largest (either in width o· height) openings remote from the cross head flue, and openings getting smaller toward the cross head flue. In constructing, all these openings should be laid up of the same depth, the amount of depth being governed by the deepest one. Loose bricks are simply set in later to the proper size of opening.

Here, with the blind flues, we are combining two essential features which have been held separate so far and are saving one set of lower collecting flues. They will give the circulation of the gases under the floor with the desired hot floor as before and at the same time take the place of under collecting flues.

In balancing the draft in each blind flue, it is only necessary to have the proper sized openings where the blind flues enter the cross head flue. The sizes of said openings (dark shaded in section *x*-*x*), first, have to be in proportion to the length of the blind or open flue behind and, second, are in some degree governed by their distance from the main draft flue entrance. The regulation of these openings can be accomplished by loose bricks, which permits final adjustment. The two open flues near the wickets, where a special strong draft is required, are directly connected with the cross head flue.

For an all perforated floor this bottom would not work so well, especially for kilns of large diameter, since there would be no regulation along the open flues, unless a construction be adopted as shown on Fig. 4*a*, which is a sectional elevation of an under-floor flue, drawn in the same scale.

This bottom has the advantages of utmost simplicity and cheapness in construction. It has the advantage of deep under-floor flues, and the open flues could fill up to the bottom of the

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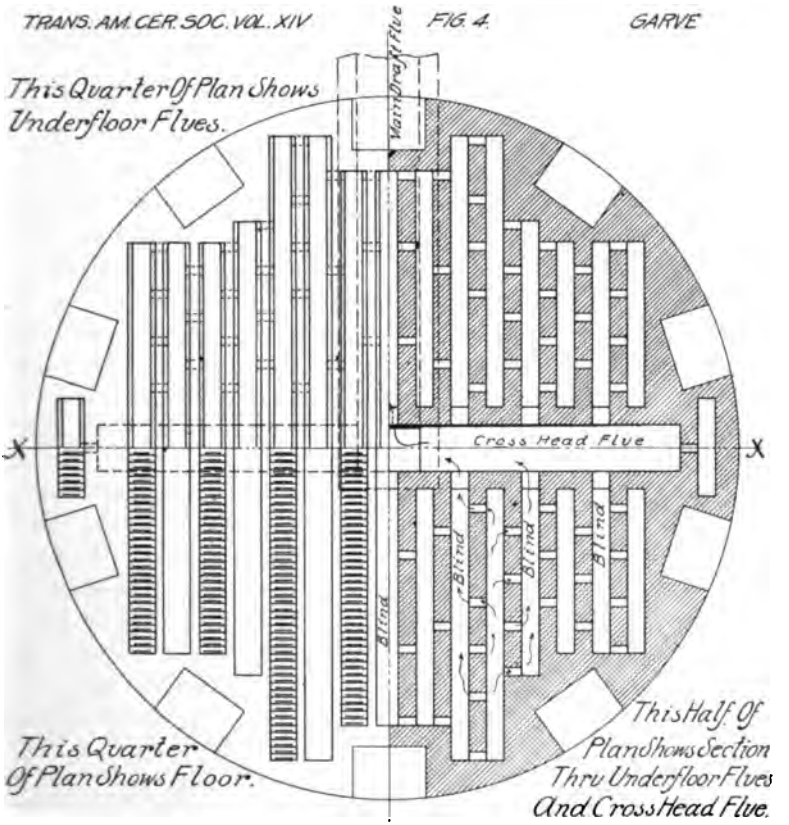

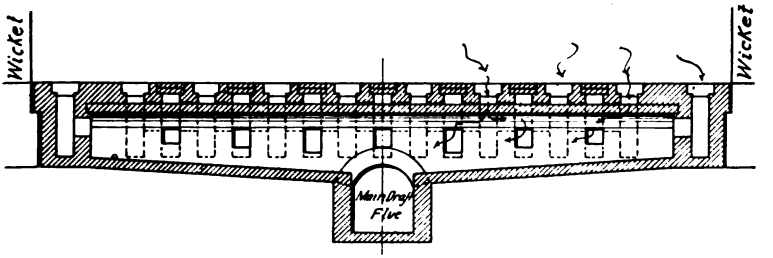

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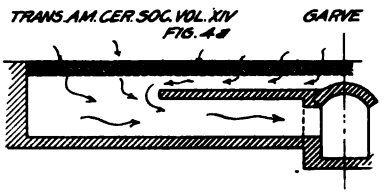
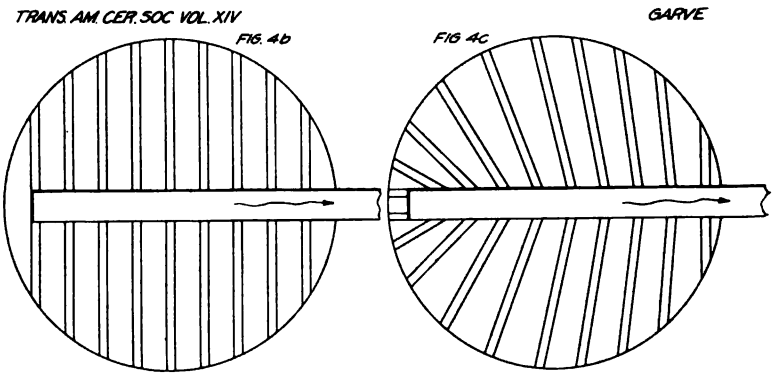


feather wall openings before it would do any harm. We have seen that in all of the previous bottoms the gases starting from the blind flues lead off through bottom openings, getting the gases soon down and away from the kiln floor proper. In this case, however, the gases have to travel close to the floor, which will result in a hotter floor and better ware upon the floor. This latter fact is the chief advantage of this type of bottom.

A simplification of this bottom (Fig. 4) would be to open up the cross head flue at one end, thus combining cross head flue and main draft flue, as shown in Fig. 4*b*; but this simplification is carried too far, since it would be difficult here to get the same draft near the stack as at the remote end. Of course, with properly dimensioned blind flue outlets good results are not impossible. The size of the kiln would play quite a rôle here.



Even with a bottom as shown in Fig. 4*c*, proposed by one designer, but little would be gained for better draft regulation or distribution over the bottom shown on Fig. 4*b*. It would only make matters more complicated. Another way would be

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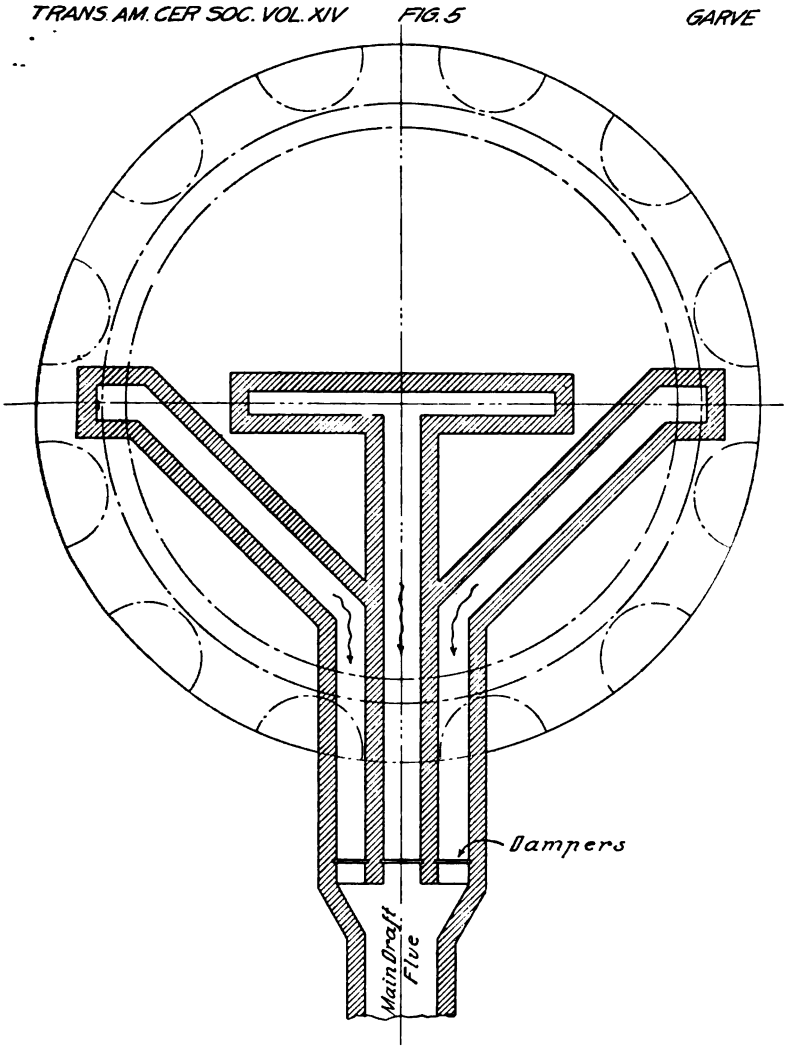

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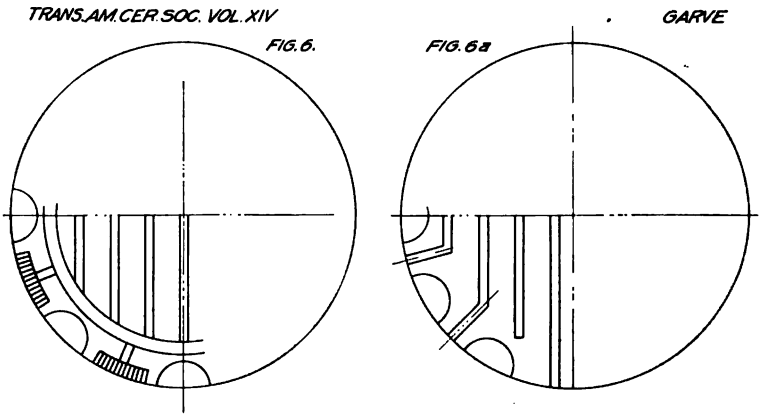
to run the cross head flue out at both ends, using two stacks; but not one of these mentioned modifications would excel or even equal the type (Fig. 4).

The kiln bottom represented by Fig. 5 shows merely a sectional plan through the lower flues under the under-floor flues; but this will suffice to get a general idea of this style of bottom.

The ring flue, shown close to the bag walls in dot and dash, is located above the section line and is level with the under-floor flues. But these could also be below. This ring, draining the outer part of the bottom, connects with the two side flues at angles of 45°. The short cross head flue takes care of the center of the kiln. Thus the gases are collected at three distinct places, carried independently to the outside of the kiln, and controlled by separate dampers until finally they all unite in the main draft flue. The idea of this arrangement is to have a dampering control of the inner and outer part o the kiln, and this idea is said to be protected by a U. S. patent. It is open to discussion, however, whether those three dampers might not become a nuisance and less effective than a properly designed bottom having a single draft control.

In some instances, however, this three-control bottom might be used to some advantage. Suppose a plant is making sewer pipe and brick, alternating frequently, this bottom might



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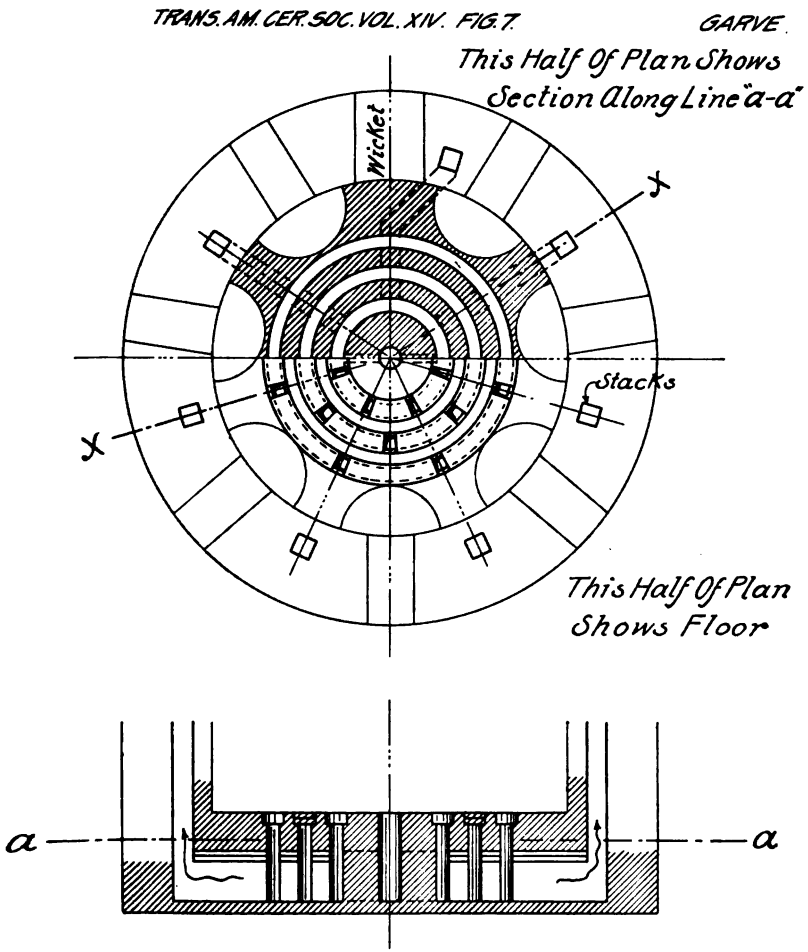

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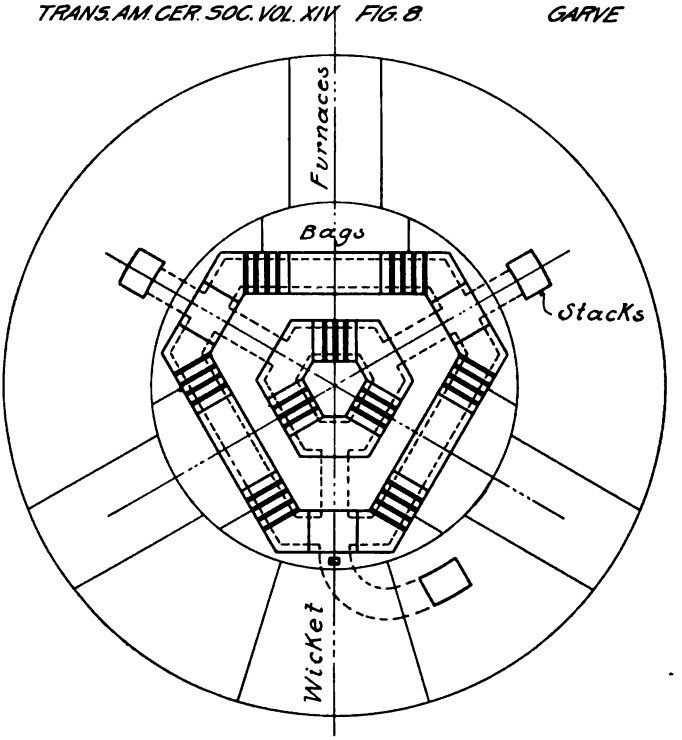
have one point in its favor in so far as it permits (without going into the interior of the bottom) stronger draft at either center or outside as may be desired.

In reference to Fig. 6, kilns with comparatively few furnaces and therefore ample space between their bags should have a special open flue between the bags as shown. It is of no consequence whether they connect with a ring flue as shown or direct with the nearest open or blind (stronger draft) flue. Where collecting flues do not naturally come between the bags, they can be angled as shown in Fig. 6*a*.

The kiln bottoms discussed so far are for ample sized industrial kilns. They might be used for kilns with inside diameters of from 20′ to 40′ or more. The larger the kiln the more economical its performance. There is much less difficulty encountered in



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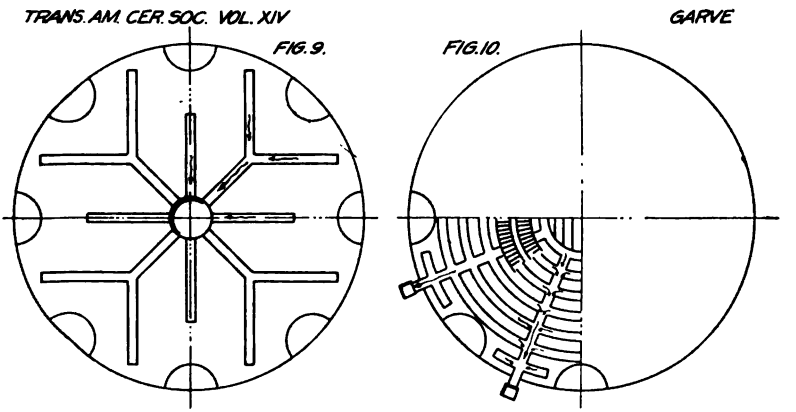
designing a proper kiln bottom for a smaller round kiln; and, though quite a variety of bottoms for this particular field could be worked out, they all would be comparatively simple and hence do not need to be discussed elaborately. The following two bottoms, however, may merit mention:

Fig. 7 has been designed for terra cotta; it is a bottle kiln and the wall stacks shown are leading the gases to the neck. The bottom consists of ring flues, radial flues, and a center hole. The ring flues are covered with special shaped tiles, and one can readily enlarge or reduce the number or size of the floor openings by simply shifting the tiles.

Fig. 8, a plan in larger scale, illustrates an elegant solution of a bottom for a small kiln with three furnaces. Such a kiln could be used for burning special shapes or as a test or experimental kiln.

Fig. 9 is a suggestion for a center stack kiln. The bottom could be used without under-floor flues or also with under-floor flues above, which would then drain through bottom openings into the flues shown.



By Fig. 10 is indicated a style of bottom which has been used largely in the past. They are perforated all over the floor. Open flues will soon fill up and it would be very troublesome in this particular case to clean the flues.

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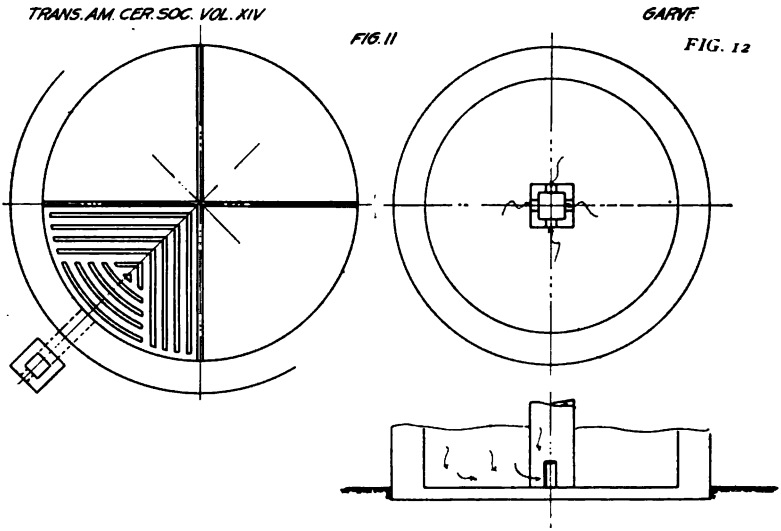
Fig. 11 illustrates a patented tile kiln. The bottom is divided up into four parts, each part having its independent flue system and stack. The stacks are placed outside the kiln walls and are provided with little furnaces for heating up the gases during the burning, thus creating a back pressure in order to hold the heat at the bottom.



The floor is very shallow, there being only one set of flues in depth; and uniform distribution of the heat in each section is obtained by different spacing of the floor blocks. Another feature of the kiln which is to be commended, although it does not concern us in this paper, is high furnace power, which enables one to burn quickly. Since the radiation loss of a downdraft kiln is from 40 per cent. to 70 per cent. of the fuel fired, any device which will shorten the time of burning will tend towards economy in fuel.

With the next bottom (Fig. 12) which finds some use in the South, the round kilns may be concluded. It is really a floor without a bottom. The bottom is set up every time in the brick to be burned, and the four openings in the center stack are to lead off the gases.

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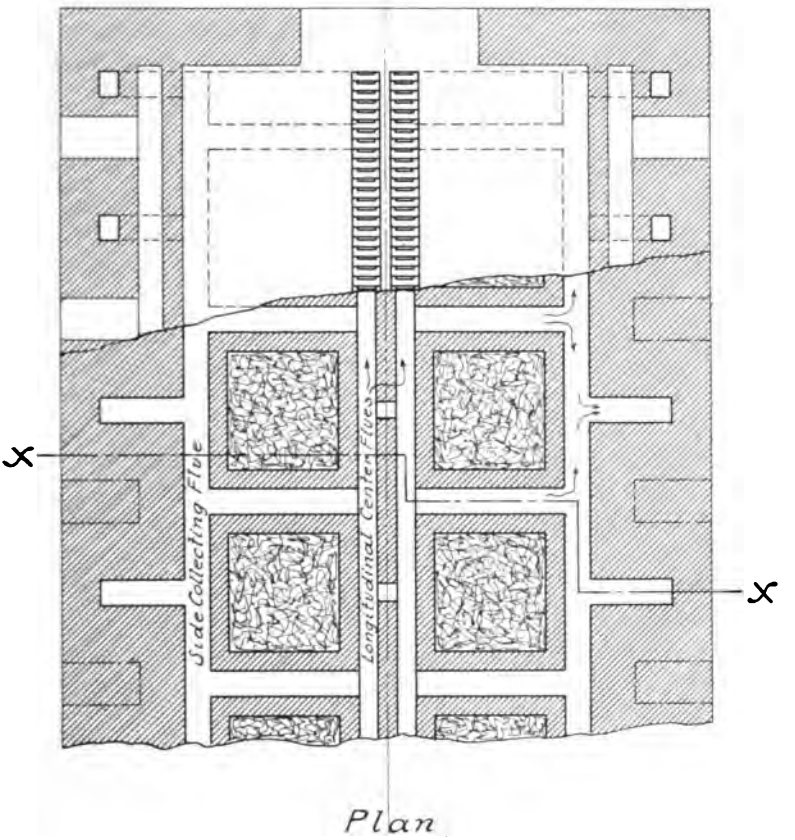
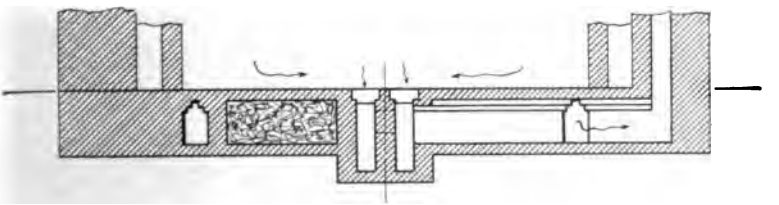
TRANS AM CER. SOC. VOL. XIV FIG. 13 GARVE



Plan



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Advantages would be: low first cost, and shallow bottom for wet ground. The inventor claims low fuel consumption.

Disadvantages would be: trouble in setting the draft flues on the temporary bottom; unequal distribution of heat; probably soft bricks in the bottom, especially on the outside.

RECTANGULAR KILNS.

Rectangular kilns are built mostly with wall stacks, and the bottoms are, as a rule, simpler than the round kiln bottoms. To discuss the advantages and disadvantages of round and rectangular kilns against each other would be outside the scope of this paper.

In Fig. 13, we have a bottom which is used extensively. It consists merely of two perforated longitudinal center flues, cross flues, and two side collecting flues. Between the latter, but toward the outside, are short connections with the wall stacks.

Frequently the side collecting flues are omitted, the cross flues connecting directly with stacks; but the side flues are a decided advantage in heating up the bottom. In setting, the two bottom courses are set across the kiln to serve as ducts to lead the gases to the center draft flues.

Little depth is required, as in most rectangular kilns, especially such as are of the wall stack type. The flues can be cleaned with little trouble after they are filled up to the entrance of the cross flues.

Sometimes such a bottom is built with three longitudinal flues instead of two, with openings in the feather walls arranged alternating to drain the center flue. Sometimes two longitudinal flues are set farther apart, leaving a 18″ brick wall or more in the center.

The bottom (Fig. 14) is the design of a well-known kiln builder. It has five longitudinal flues with perforated floor, and cross flues connect the longitudinal flues with the side collecting flues and thence to the stacks. It has greater floor perforation than the preceding kiln; but the tendency of later kiln construction has been toward less open floors. There is complete circulation of the gases under the kiln floor which is a good feature of the kiln.

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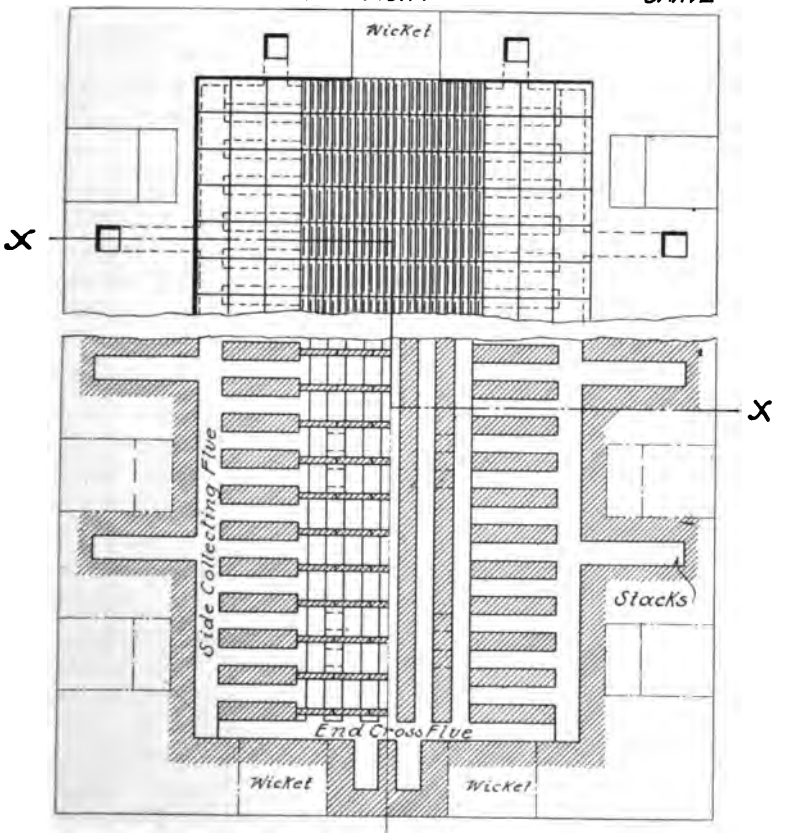
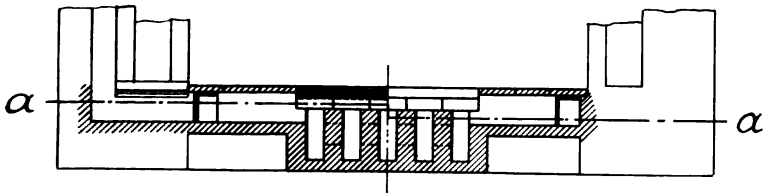
TRANS. AM. CER. SOC. VOL. XIV FIG. 14 GARVE



Floor Plan and Sectional Plan 'a-a'



Section x-x

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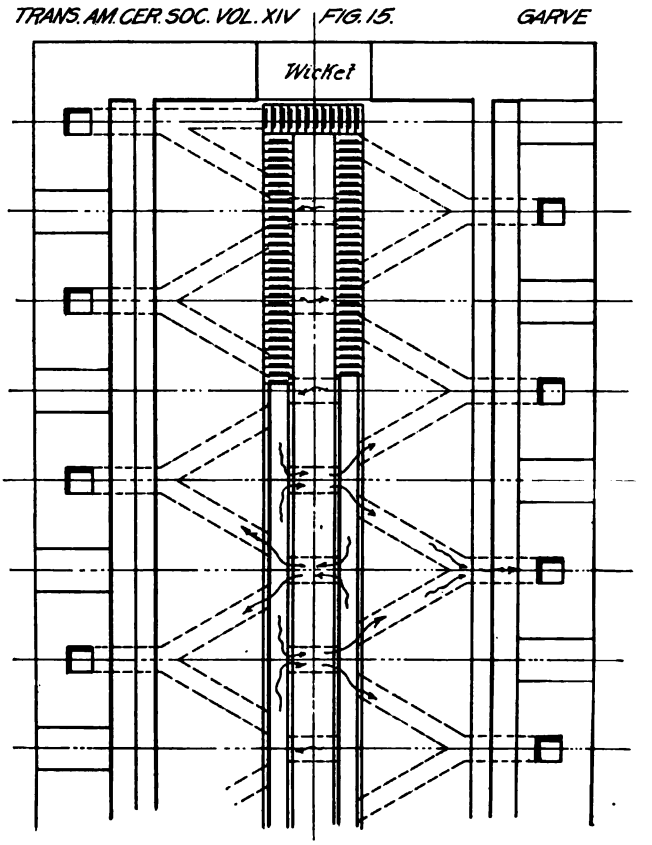

Floor Plan

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Special attention should be given to the ends of a rectangular kiln bottom. In the last mentioned bottom there are two stacks within the end walls. These draw from a deep end cross flue, one at each end, to get sufficient draft there. On the previous bottom, the side wall stacks are placed close to the ends, in fact, as close as possible to accomplish this result.

Fig. 15 is the suggestion of a bottom for a kiln with a different arrangement of furnaces and stacks. On the previous kilns, the furnaces were opposite each other and also the stacks opposite each other. In this case, the furnaces are opposite the stacks. The object is to get a good heat distribution right from the start.

The bottom, it will be seen, allows considerable circulation of the gases, avoiding unnecessary friction around corners. The comparatively strongest draft, as can be seen, will prevail away from the furnaces, and in this case the openings in the center feather wall are essential.

Fig. 16 is a bottom of recent date, developed by P. J. Laubscher, of New Galilee, Pa., who has applied for a U. S. patent. The gases pass through 5″ openings in the floor, three being in every other cross flue. The cross flues are alternatingly open and blind, and the gases, after having entered an open cross flue, have to make a turn to reach the next blind flue. These blind flues open alternatingly into the left and right main flue. The wall stacks are above these main flues.

It will be seen that there is ample circulation under the floor, resulting in a hot bottom. It will also be noticed that the side flues or main flues are unusually far outside and are immediately below the furnaces. The object of this is to heat up the gases shortly before they reach the stacks, to give a strong pull. The location as shown, however, will be well in view of starting fires in the ash pits during the water-smoking, for it is during this period that a strong draft is required but seldom available.

The advantages of the kiln as claimed by the inventor are: solid floor, perfect distribution of heat over the floor, complete circulation under the floor, shallow bottom, strong draft especially during water-smoking, hard burns to the floor, quick burns, and low fuel consumption.

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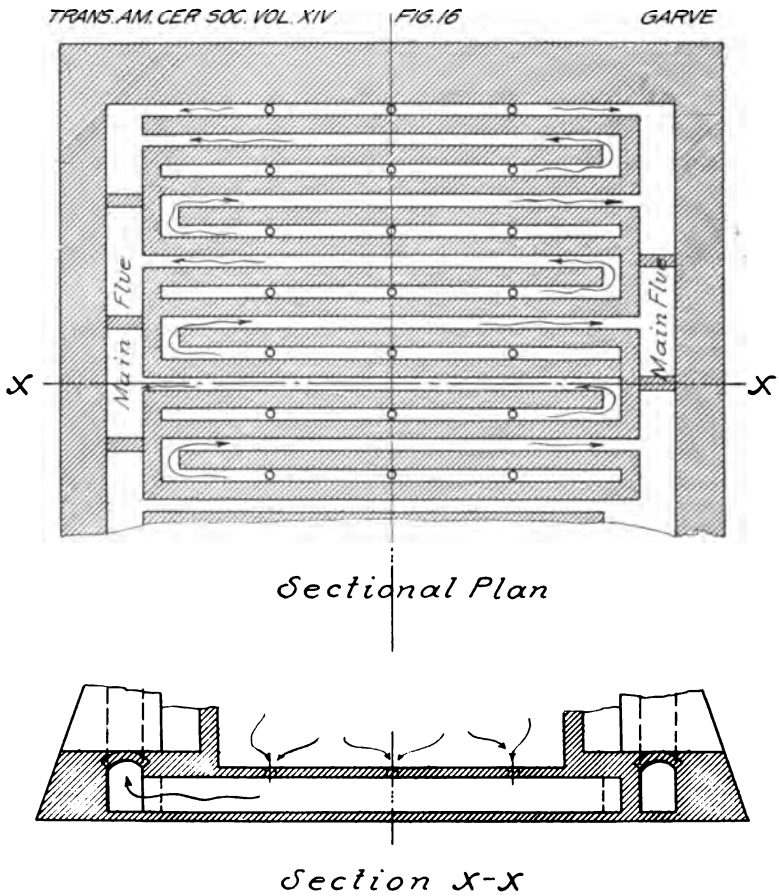

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It would seem as if the extension of the floor flues under the bags and the main draft flue under the furnaces would lead to some loss of heat through heating up the gases carried out by the stacks. In the water-smoking stage, the advantage of this heating up in giving strong draft far exceeds any loss in heat. In the final high fire stage, when we work with close dampers, the loss will be small and it seems to us will be more than offset by the back pressure which the expansion of the gases in the draft flue will give. It virtually will have the effect of dampering the kiln at the floor outlets, which we would like to do if such dampering were possible.

Fig. 17 is not a bottom for a multiple stack kiln. There are two stacks outside of the kiln, one at each end. These stacks are drawing from the main draft flues, which latter have cross flues connected to the center flues. As seen, these cross flues are narrowest near the stack and are getting wider toward the other end. Their increase in width should be proportioned to the increase in friction to the gases. Both sides being constructed alike, only reversed, it would be of but little consequence if a somewhat stronger pull should prevail through the cross flues nearest to the stack, since the conditions would be contrary on the other side of the kiln bottom. In other words, the cross flue on one side nearest the stack and having the strongest pull will be adjacent to the cross flue on the other side farthest from its stack and having the weakest pull, and both are pulling from the floor in the center. Thus the combined drafts of both sides are equal at every point the length of the kiln. This equalizing action of strongest and weakest pull is an essential feature of this bottom that deserves mention.

The location of the furnaces has not been indicated on this drawing, since this style of bottom would and could be independent of their number and location.

Some modification of this bottom can be made by placing the cross flues opposite each other, but then they should be arranged between furnaces and starting with two opposite cross flues close to the wickets.

The bottom, Fig. 17, can be used to special advantage for improving old kilns with faulty bottoms, since no side walls

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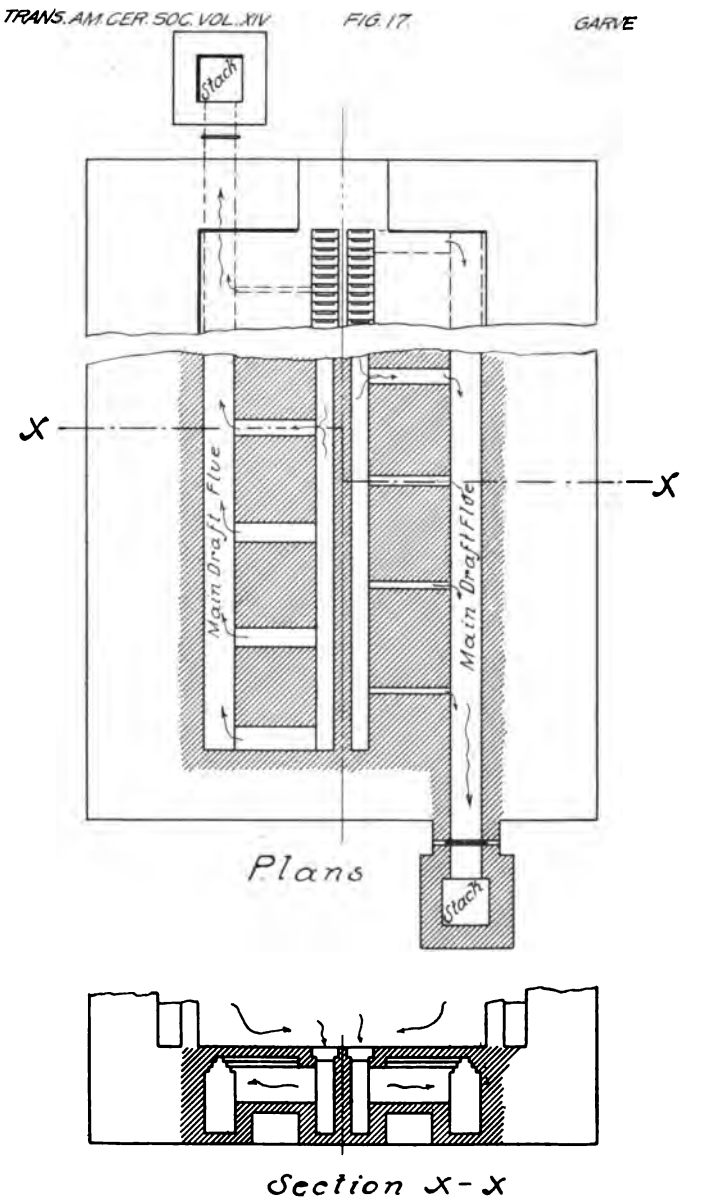

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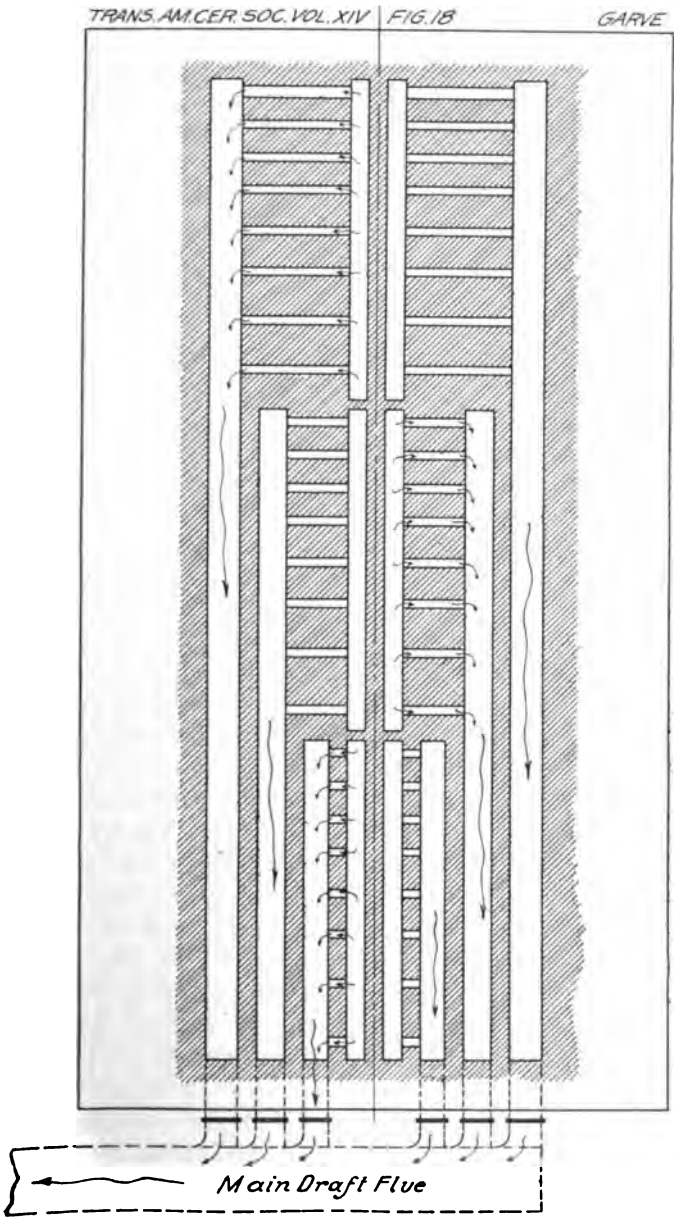

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would have to be disturbed. The same will hold for changing updraft kilns to downdraft kilns.

In Fig. 18 we have a bottom for only one outside stack. Here again we have two perforated center flues close together. These flues are divided up into three distinct parts by two cross walls. The part nearest to the main draft flue or stack drains its gases to the adjacent two side collecting flues. The next two side collecting flues, being farther out, take care of the center part of the kiln, and the outer two side collecting flues carry the gases from the remote end of the kiln to the main draft flue. These latter flues are, therefore, the widest and the first mentioned or shortest side collecting flues are the narrowest. Also, within each part some regulation should be provided, and this is done by spacing the cross flues the closer together the farther they are from the main draft flue or stack.

This bottom insures good circulation and could favorably be used under the same conditions as described before, but for very long kilns a double stack or wall stack kiln would be better.

Fig. 19 may be discussed briefly. It represents the bottom of a patented kiln, the principle of which is to first convey the furnace gases through flues below the floor and then to let them rise out of bags at the opposite side. Thus by conduction, the floor will become well heated up, the intensity of the heating depending upon the thickness of the floor or flue coverings.

The gases, after the rise within the bags and their final downward motion, are taken out at the ends through openings above the floor, leading to the wall stacks. The kiln is built both round and rectangular and has been largely used in burning tile. In order to get proper heat distribution, flues are made in the set bricks leading to the openings in the wall stacks.

The floor being thin, carrying the weight, and receiving the first and highest heat, will require frequent repairs. Of course, there is no trouble with dirt or sand getting into the flues, and the result is an always clean bottom. Doubtless, no other bottom described can ever be made as hot as this type, and good hard burns could be obtained for the ware on the floor.

The original kiln, especially the rectangular, was limited in size on account of the stacks being in the ends of the kiln.

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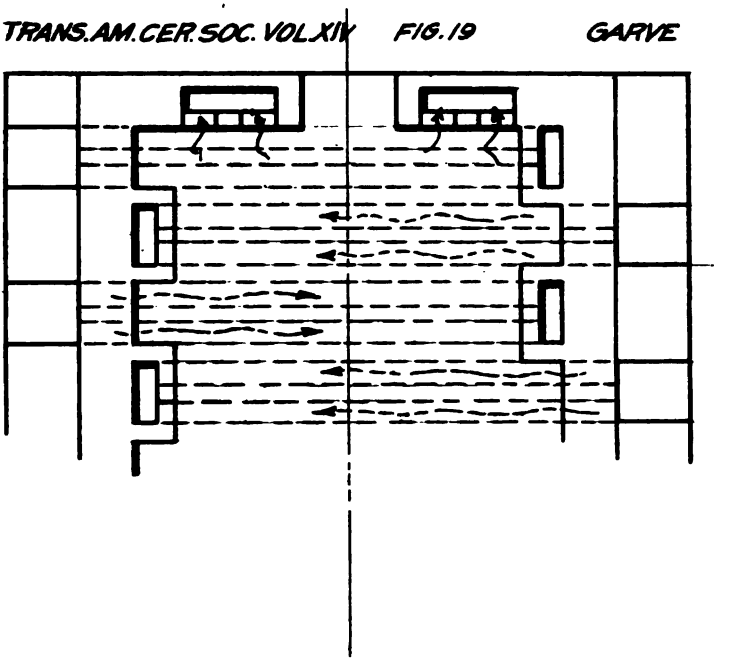

A modification of this inserts a perforated floor cross flue alternating with each pair of furnaces. This cross flue connected with wall or outside stack in or along the side walls of the kiln. Thus the kiln could be divided into about eight-foot sections, each controlled by a wall stack. In this way the kiln can be built any length. The draft flue, being between two furnace flues and on the same level, heats up quickly and gives strong draft in the early stages of the burning as well as later.

The kiln would find much wider use were it not for the trouble in keeping up the under-flues. It has a solid floor and the ware can be burned equally hard on top and bottom. The time for burning is shortened, since the heat has to travel either up or down only about one-half the height of the setting. The modification above mentioned insures strong draft at the start.

CONCLUSION.

This may suffice to show that there is quite a variety of downdraft kiln bottoms possible and justified. Each bottom

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has its merits and weak points, and only by carefully balancing them against each other should the final conclusion for the particular case be derived.

Not all of the bottoms in existence, covered by patents or otherwise worked out by men of theory and practice, could be included in this paper; and not everything from a practical as well as a theoretical standpoint could be pointed out, for that could not be done within the scope of a paper but would fill the pages of a book, or at least a pamphlet.

The bottoms which have been incorporated are noteworthy and modifications can be developed therefrom to suit a more particular case. All the bottoms we have shown, except two or three marked "suggestions," are in practical use together with numerous modifications of each. The tendency of development for brick burning is toward a solid floor. Drain tile uses a perforated floor but semi-solid floors are coming in, and it has been learned that tile can be burned on such a floor as well as bricks. Sewer pipe uses the fully perforated floor and will probably continue to do so on account of full glazing required on the inside of the pipe. Fire-proofing may profitably abandon the fully perforated floor and adapt a floor with less openings but complete circulation under the floor.

The consensus of opinion and practice is that the floor with fewer and smaller openings distributes the heat better over the floor and gives better burns on the bottom than the fully perforated floor with wide openings. The floor acts as a damper; and the nearer the ware we can introduce a damper, the better the heat distribution throughout the kiln and the more uniform the burn.

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COLORS PRODUCED BY NICKEL OXIDE IN CERAMIC MIXTURES CONTAINING ZINC.

By FORREST K. PENCE, Zanesville, Ohio.

Introduction.—There has come to my attention considerable evidence from various sources that nickel oxide in ceramic mixtures containing zinc produces colors other than brown —notably blue. There has always been some doubt concerning these results, the presumption being that the blue color might be due to the presence of traces of cobalt.

In Vol. VI, p. 195, Transactions A. C. S., opinions are given concerning the coloring action of nickel; and Geijsbeek states that Le Chatelier and Chapuy obtained violet, blue, green, yellow, red, and brown, from nickel in oxidizing fire. My own experience with nickel oxide in commercial work indicates to me that considerable range of color is possible with nickel.

Preparation of Nickel Oxide.—I have undertaken in the following investigation to determine the coloring action of nickel oxide that has a very high degree of purity. Therefore, the nickel oxide used was prepared.

In Baker's Catalog of "Analyzed Chemicals," the only salt of nickel which is listed as being free from cobalt is nickel ammonium sulphate. To a solution of this salt was added a solution of Baker's ammonium carbonate. The precipitate of basic nickel carbonate was filtered off and washed free from sulphates. The precipitate was then dried and ignited to constant weight. The dark, grayish powder obtained is probably a mixture of NiO and Ni_2O_3. It will be considered as NiO for the purpose of this investigation.

Preparation of Stain.—NiO, both prepared and commercial, was first introduced into mixtures of zinc oxide and flint, the mixtures ground together in an agate mortar and fired to cone 10. The mixtures were as shown in Table I.

The blue color developed above is of a light Persian hue. That from the commercial oxide is a trifle darker than that from the prepared.

It is seen that the blue color is developed only in those mixtures containing both zinc oxide and flint. It would seem that this color action depended upon the formation of a zinc silicate compound in some sort of combination with the nickel.

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TABLE I.

Stain	Formula				Batch				
	NiO		ZnO	SiO_2	Color	NiO		Zinc oxide	Flint
	Prepared	Commercial				Prepared	Commercial		
A.....	..	..	1.0	1.4	White	...	...	8.1	8.4
B.....	..	0.20	0.80	1.4	Blue	...	1.5	6.48	8.4
C.....	0.20	..	0.80	1.4	Blue	1.5	...	...	8.4
D.....	1.0	..	..	1.4	Nickel green, brownish tint	7.5	...	...	8.4
E.....	..	0.20	0.80	...	Nickel brown	...	1.5	6.48	...

SERIES I.

In order to study the color effects of nickel in ceramic mixtures with increasing amounts of zinc, a glaze series was used in which the base glazes are the same as those used by Bryan in his study of the "Action of Chromium Oxide in Glazes Containing Zinc," Vol. X of the Transactions A. C. S. To this end the four glazes representing the extremes of the series were weighed out, ground in ball mill for 2 hours, dried, and used for blending in the compounding of the series. These four glazes were as shown in Table II.

TABLE II.

Glaze	G	G_4	O	O_4
K_2O.....	0.25	0.25	0.25	0.25
CaO.....	0.30	0.30	0.14	0.14
BaO.....	0.45	0.45	0.21	0.21
ZnO.....	0.00	0.00	0.40	0.40
Al_2O_3.....	0.30	0.30	0.30	0.30
SiO_2.....	2.0	2.0	2.0	2.0
NiO.....	..	0.02	..	0.02
Feldspar.....	139.25	139.25	139.25	139.25
Whiting.....	30.0	30.0	14.0	14.0
Barium carbonate.....	88.65	88.65	41.37	41.37
Zinc oxide.....	..	..	32.4	32.4
Raw clay.....	12.9	12.9	12.9	12.9
Flint.....	24.0	24.0	24.0	24.0
Nickel oxide.....	..	1.5	..	1.5
Equivalent weight.....	294.80	296.30	263.92	265.42

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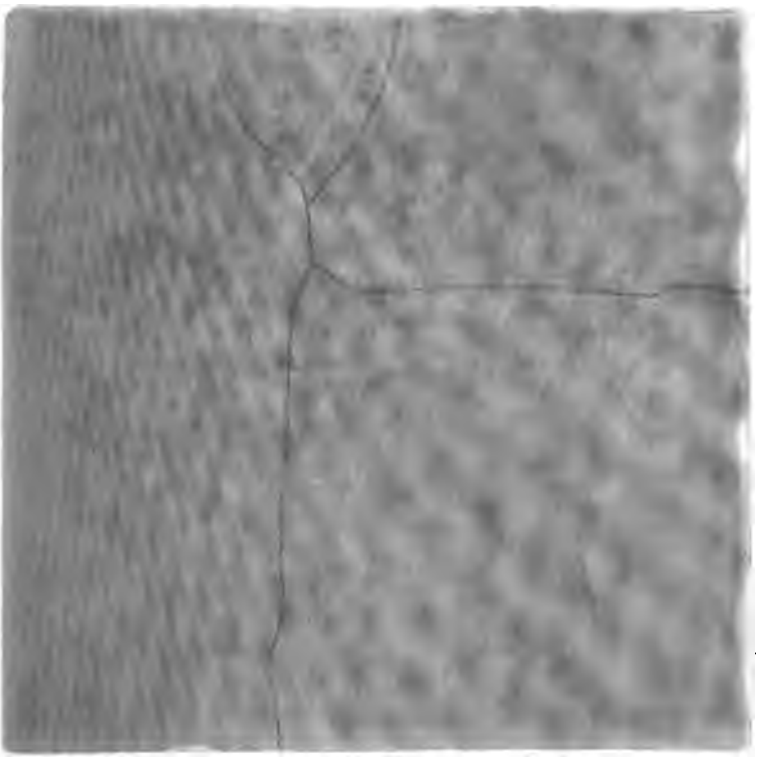

Blue Produced by Use of Nickel Oxide

$$\left.\begin{matrix} 0.25\ K_2O \\ 0.14\ Ca\ O \\ 0.21\ Ba\ O \\ 0.40\ Zn\ O \end{matrix}\right\} \text{Series I, } O_3 \quad 0.30\ Al_2O_3 \quad 2.0\ SiO_2$$

$$0.15\ Ni\ O$$

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The four base glazes were blended dry in the ratio of their equivalent weights to produce the glazes shown in Table III.[1] The blends were ground and dipped onto small wall tiles ($^3/_4'' \times {}^3/_4''$). The entire series was then placed upon a fire-clay plate of dimensions $6'' \times 8''$ and fired in a saggar to cone 5 in a commercial downdraft kiln. A uniform firing treatment of the series was thus assured. Tiles were placed in two kilns, each kiln containing a duplicate series, as a check on the influence of the fire.

Each series gave practically the same results. Table III shows the series in terms of empirical molecular formulae and indicates the color effects obtained.

The colors simply increase in intensity with increase of NiO until they are quite strong with 0.20 equivalent.

It will be noted that a rather sharp change from brown to reddish purple occurs in the K's and L's.

In the M's there seems to be a struggle for the mastery, so to speak, between the elements producing purple and those producing blue, both colors being in evidence with the blue predominating at the edges.

In the N's we have a distinct blue which is maintained in the O's with occasional appearance of greenish hues at the edges.

SERIES II.

In order to check these results and to study further the color change from brown through purple to blue, a second series was constructed which should cover the area of color change from brown to blue with more gradual increase of ZnO. The NiO used was also prepared independently of that used in the first series in order to check the results from the oxide.

The very same method of preparation and treatment was used in this series as has been described in detail in the first series.

The series and results are given in Table IV.

It is seen that the results in Series I are practically duplicated, with the area of color change or transition more fully shown.

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[1] It appears from Bryan's table, Vol. X, bottom of p. 126, of the Transactions, that Bryan did not calculate the number of parts to be blended, but erroneously used the figures for equivalents instead.

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TABLE III.—Series I.

ALL GLAZES CONTAIN 0.30 Al_2O_3 2.0 SiO_2.

	G	H	I	J	K	L	M	N	O
K_2O	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
CaO	0.30	0.28	0.26	0.24	0.22	0.20	0.18	0.16	0.14
BaO	0.45	0.42	0.39	0.36	0.33	0.30	0.27	0.24	0.21
ZnO	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
	G_1	H_1	I_1	J_1	K_1	L_1	M_1	N_1	O_1
0.005 equivalent NiO	Brown	Brown	Brown	Brown	Change to purple	Reddish purple	Change to blue	Blue	Blue
	G_2	H_2	I_2	J_2	K_2	L_2	M_2	N_2	O_2
0.010 equivalent NiO	Brown	Brown	Brown	Brown	Change to purple	Reddish purple	Change to blue	Blue	Blue
	G_3	H_3	I_3	J_3	K_3	L_3	M_3	N_3	O_3
0.015 equivalent NiO	Brown	Brown	Brown	Brown	Change to purple	Reddish purple	Change to blue	Blue	Blue
	G_4	H_4	I_4	J_4	K_4	L_4	M_4	N_4	O_4
0.020 equivalent NiO	Brown	Brown	Brown	Brown	Change to purple	Reddish purple	Change to blue	Blue	Blue

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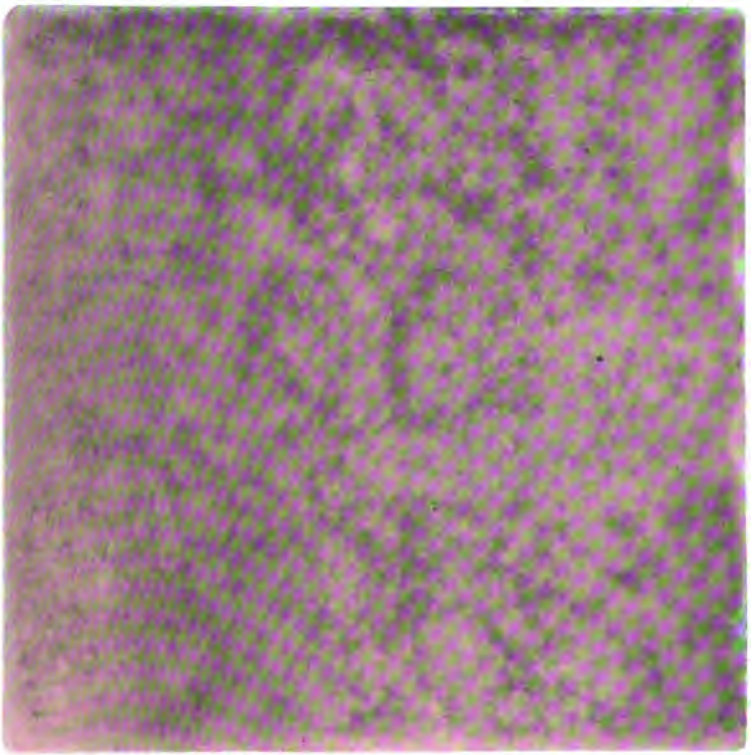

Purple Tint Produced by Use of Nickel Oxide

$$\left.\begin{matrix} 0.25\ K_2O \\ 0.20\ Ca\ O \\ 0.30\ Ba\ O \\ 0.25\ Zn\ O \end{matrix}\right\} \quad \text{Series I, } L_3$$
$$0.30\ Al_2O_3\ \ 2.0\ Si\ O_2$$
$$0.15\ Ni\ O$$

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TABLE IV.—Series II.

ALL GLAZES CONTAIN 0.30 Al_2O_3 2.0 SiO_2.

	J	K	KL	L	LM	M	MN	N
K_2O	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
CaO	0.24	0.22	0.21	0.20	0.19	0.18	0.17	0.16
BaO	0.36	0.33	0.315	0.30	0.285	0.27	0.255	0.24
ZnO	0.15	0.20	0.225	0.25	0.275	0.30	0.325	0.35
	J_1	K_1	KL_1	L_1	LM_1	M_1	MN_1	N_1
0.005 equivalent NiO	Brown	Change to purple	Brownish purple	Reddish purple	Reddish purple	Change to blue		Blue
	J_2	K_2	KL_2	L_2	LM_2	M_2	MN_2	N_2
0.010 equivalent NiO	Brown	Change to purple	Brownish purple	Reddish purple	Reddish purple	Change to blue		Blue
	J_3	K_3	KL_3	L_3	LM_3	M_3	MN_3	N_3
0.015 equivalent NiO	Brown	Change to purple	Brownish purple	Strong reddish purple	Strong reddish purple	Change to blue		Blue
	J_4	K_4	KL_4	L_4	LM_4	M_4	MN_4	N_4
0.020 equivalent NiO	Brown	Change to purple	Brownish purple	Strong reddish purple	Strong reddish purple	Change to blue		Blue

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SERIES III.

It had been noted that certain greenish tints were pronounced, particularly near the edges where the glaze was thinnest and, perhaps, where tendency to become shiny had progressed farthest. I had also observed a dark green obtained from a glaze rather high in ZnO and NiO and low in Al_2O_3 and SiO_2. To investigate this point another series was constructed in which the Al_2O_3 and SiO_2 were gradually reduced, the O. R. remaining constant, and in which a higher content of NiO was used. This series is shown in Table V.

TABLE V.—Series III.

ALL GLAZES HAVE SAME RO.

RO { 0.15 K_2O, 0.20 CaO, 0.20 BaO, 0.45 ZnO

	P	R	S	T
Al_2O_3	0.30	0.25	0.20	0.15
SiO_2	2.0	1.83	1.66	1.5
0.010 equivalent NiO	P_1	R_1	S_1	T_1
0.020 equivalent NiO	P_2	R_2	S_2	T_2
0.030 equivalent NiO	P_3	R_3	S_3	T_3
0.040 equivalent NiO	P_4	R_4	S_4	T_4
0.050 equival nt NiO	P_5	R_5	S_5	T_5
0.060 equivalent NiO	P_6	R_6	S_6	T_6

The results do not show any important color change with reduction of Al_2O_3 and SiO_2. The color throughout remains blue with noticeable tendencies toward greenish hues.

The glaze itself shows an interesting development in that a rather coarse crystalline structure becomes apparent at cone 5 with reduction of alumina and silica to 0.25 Al_2O_3 1.83 SiO_2 and lower.

In those showing crystallization the strong greenish blue color is found following the crystal development. Along the extreme edges of the tiles, the glaze tends to be bright, and the crystallizing material seems to have been drawn away by the massive crystal growth of the inner portion. The color of the

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portion about one-sixteenth inch wide around the edges is light to distinct brown.

The following bright glazes were fired at cone 02.

$$\left.\begin{matrix}0.45\ PbO\\0.10\ K_2O\\0.45\ ZnO\end{matrix}\right\}\ 0.175\ Al_2O_3\left\{\begin{matrix}1.50\ SiO_2\\0.01\ NiO\end{matrix}\right.$$

The color produced was a greenish blue.

$$\left.\begin{matrix}0.85\ PbO\\0.15\ K_2O\end{matrix}\right\}\ 0.20\ Al_2O_3\left\{\begin{matrix}2.0\ SiO_2\\0.01\ NiO\end{matrix}\right.$$

The color produced was the familiar nickel brown. To the glaze batch for the latter formula was also added:

$$1\%\ \text{of stain C,}\ \left\{\begin{matrix}0.020\ NiO\\0.^{c}0\ ZnO\end{matrix}\right\}\ 1.40\ SiO_2$$

The result was a nickel brown.

As a further refinement of the preparation of NiO, a portion was subjected to the potassium nitrite method for separation of cobalt as given by Noyes, Vol. XXX, J. A. C. S. A slight cloudiness was produced upon addition of the KNO_2 to the nickel solution. The solution was filtered and nickel hydroxide precipitated by addition of NaOH to the clear filtrate. This was washed and ignited to the oxide. This oxide can not contain more than 0.20 of 1 per cent. of cobalt.

In Glaze O4 this would be 0.003 part of cobalt oxide to the batch or 0.00004 equivalent.

Ten times this amount of cobalt introduced into Glaze O produces a very slight bluish tint.

The nickel oxide from the potassium nitrite treatment gives, in Series I, the same results as does the original prepared oxide.

CONCLUSION.

There remains no doubt that, in Series I, the transition from brown with 0.15 ZnO, through strong reddish purple with 0.25 ZnO, to dark blue with 0.35 ZnO, is due to the action of nickel oxide in the presence of increasing amounts of zinc. What this action may be remains an unanswered question. I should hesitate to presume that it is due to an oxidizing action, as Bryan maintains in the case of Cr_2O_3 in the presence of zinc. The blue was obtained in the case of stain C under reducing conditions.

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I think it probable that the color obtained is a property of some combination consisting essentially of nickel, zinc and silica.

DISCUSSION.

Prof. Binns: An instance which recalled itself to my memory was a discussion on crystal glazes, in which a crystal glaze containing nickel was described as giving blue crystals on a buff ground. The question was raised why nickel should produce a blue color, and it was suggested that the blue might be due to a trace of cobalt.

Mr. Pence shows that zinc and nickel may have been responsible for the color.

Mr. Pence: The bright glaze used first consisted of a glaze containing high lead and no zinc in which was obtained a distinct nickel brown color. In the glaze containing 0.45 PbO and 0.45 ZnO, a greenish blue was obtained in which the greenish color was more pronounced than in the leadless mattes containing high zinc.

Prof. Binns: Any attempt to introduce boric acid?

Mr. Pence: Not in this experiment.

Prof. Orton: Mr. Chairman, I want to ask Mr. Hottinger whether in those nickel blues that he produced some years ago, he didn't take steps to get the nickel oxide free from cobalt.

NOTE WRITTEN AFTER READING THE PAPER.

Mr. Hottinger: I made some experiments which confirm the statement that nickel oxide yields a blue color. I purified some nickel nitrate and got it free from cobalt and then used the pure oxide in a crystal glaze. This produced a blue crystal. I then tried to produce a crystal similar in color with cobalt oxide by adding the oxide in varying amounts, but was unable to produce the same effect that nickel oxide gave in the crystal glaze. In order to get a blue crystal of some depth of color, I had to use very much more cobalt oxide than I found in the nickel and then the color of the finished piece was entirely different. With the nickel, I had blue crystals on a light fawn colored ground, or, if the glaze happened to be transparent, a blue crystal in a typical nickel brown glaze. With the cobalt, I could only get a blue glaze with the crystals in a darker blue color.

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I notice Mr. Pence speaks of a green color he observed in certain of his glazes. I also have observed this color in some glazes. The one which I recall had the following composition:

$$\left.\begin{matrix} 0.30\ CaO \\ 0.15\ K_2O \\ 0.30\ Na_2O \\ 0.15\ MgO \\ 0.10\ ZnO \end{matrix}\right\} \left\{ 0.20\ Al_2O_3 \right\} 1.60\ SiO_2$$

This glaze with small amounts of nickel oxide produced light greenish colors.

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DRYING DEFECTS IN SOME CRETACEOUS CLAYS OF THE GREAT PLAINS REGION OF CANADA.[1]

By JOSEPH KEELE, Ottawa, Can.

LOCATION AND CHARACTER OF THE CLAYS.

Of 120 samples of clays and shales collected recently by Professor Heinrich Ries and the writer in the Great Plains region of Canada, 28, or about 23 per cent., cracked in air drying.

These defective clays occur principally in the upper part of the Cretaceous, in the formations known locally as the Belly River and Edmonton, but they also happen in the Laramie, or Lower Tertiary.

The rocks that comprise these formations are wide-spread in the provinces of Saskatchewan and Alberta. They are massive clays, soft shales, friable sandstones, and lignites. Many of these beds are lenticular in character, so that overlapping and lack of continuity of the various members of a series is common. Hence, vertical sections often vary widely within short distances. The beds over the greater part of the area appear to be undisturbed from the position in which they were originally laid down, and the present surface of the region reflects in general the attitude of the underlying rocks.

As the greater part of the surface is covered by a sheet of drift materials of varying depth, the Cretaceous clays are mostly to be seen on the walls of stream valleys, or along the escarpments of the infrequent uplands. Even in these exposed situations, however, the rocks are frequently concealed, owing to their softness and the ease with which they weather down into soils. Many of the best exposed sections are obtained in the fresh cuttings of the railways that are being rapidly constructed in all directions throughout this region.

Along the western margin of the Great Plains, the Cretaceous sediments have become involved in the processes of mountain building, and most of the foothills that flank the eastern front of the Rockies are built of them.

Although we found in two instances that shales collected from the foothills cracked very badly, all the other samples taken

[1] Published by permission of the Director of the Geological Survey of Canada.

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from this area had good drying qualities. The shales and clays of the Plains are found well situated for ease of working and transportation, being of immense economic importance if they can be utilized. In several cases it has happened that the most desirable beds of the series to the clay worker, *i. e.*, those from which vitrified wares might be made, were the ones that gave the greatest or the only trouble by cracking.

Many of these shales that have drying defects may be manufactured dry press for use as facing bricks, but it is impossible to use them for the many important structural wares which involve the use of the wet moulded processes.

In Table I will be found analyses of several of the clays described in this paper. They were made by G. E. F. Lundell. The greater part of these clays is made up of quartz grains of varying degrees of fineness, as many clays are, and the chemical analysis furnished no clue to their erratic behavior.

TABLE I.—ANALYSES OF CANADIAN CLAYS THAT CRACKED IN DRYING.

	No. 2	No. 3	Bentonite from Camrose
Total silica, SiO_2	74.25	65.23	69.14
Alumina, Al_2O_3	14.29	18.60	14.50
Oxide of iron, Fe_2O_3	2.89	2.97	2.56
Lime, CaO	0.37	0.66	2.45
Magnesia, MgO	Trace	0.64	1.14
Potash, K_2O	2.52	2.40	0.19
Soda, Na_2O	1.19	2.23	1.26
Loss on ignition	4.21	7.30	7.71
	99.72	100.03	98.95
Supplemental determinations			
Organic carbon	not determined	1.44	not determined
Carbon dioxide, CO_2	none	0.42	0.52
Sulphur trioxide, SO_3	none	none	1.70
Hydrous silica	0.43	0.51	21.03
Sulphur	none	none	not determined

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PRELIMINARY WORK.

During the progress of the laboratory work on the samples of these clays collected in the field, the writer was confronted with the difficulty of preparing test pieces from them for the purpose of observing their behavior under fire. The clays absorbed a great deal of water in tempering, afterwards forming a stiff, pasty mass, which was tough and sticky and hard to work. Shortly after being set to dry, the molded shales cracked, even small test pieces cracking badly at the ordinary laboratory temperature. The surface of a full sized brick readily became dry and developed a perfect network of cracks, which deepened and widened as drying progressed, while the inside remained moist for several days.

The use of substances which would coagulate the clay was tried to cure this cracking, care being taken to use materials which were cheap and readily available, so that if the remedy were successful it could be used on a commercial scale. Of the various acids and alkalis tried, common salt to the amount of 1 per cent. seemed to give the best results. The salt kept the surface of the bricklets moist while the water was working its way out of the body. Full-sized bricks made from some clays thus treated would dry safely at ordinary room temperature, but many clays would not. A few of the salted clays would stand even moderately fast drying. Furthermore, the stickiness and soap-like qualities of the clays were not ameliorated to any appreciable extent by the mixture.

The next method which suggested itself was the use of non-plastic materials like sand or grog. River sand, ground quartz and calcined clay were successively used for grog. These were added to the clays in varying amounts up to 50 per cent.

The mixtures with sand failed in every respect, and although the grogged clay could be safely dried in some instances and burned to a good body, the bad working qualities of the raw clay were still in evidence.

Professor Orton,[2] who was experimenting on some clays of

[2] Edward Orton, Jr., "Experiments on the Drying of Certain Tertiary Clays," Trans. A. C. S., Vol. XIII.

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the Edmonton series at the same time as the writer, was unsuccessful in overcoming their drying defects by the use of either chemical coagulants or additions of non-plastic materials.

PREHEATING EXPERIMENTS.

There remained then the method devised by Professor A. V. Bleininger for treating clays that cracked in drying by preheating the raw clays at various temperatures. Preheating experiments were done on several of our clays, and the results arrived at seem to prove that this is the best method, so far, for dealing with the difficulty.

The data for six samples of clay from localities widely apart are here given. Clays of these types may be expected to occur frequently in other localities throughout the region we are dealing with. Numbers 1 and 2 are used for making dry pressed bricks, the other samples are from unused deposits.

TABLE II.—CLAYS HEATED IN ROTARY DRUM.

No.		400° C. 15 min.	450° C 15 min.	500° C. 15 min.	500° C. 30 min.	550° C. 15 min.	550° C. 30 min.
1	Drying at 65° C.	..	..	..	Bad	Improved	Good
	Drying at 30° C.	..	..	..	Bad	Good	Good
	Plasticity	..	..	..	Good	Fair	Low
2	Drying at 65° C.	Good	..	..	..	.....	..
	Drying at 30° C.	Good	..	..	..	.....	..
	Plasticity	Fair	..	..	..	.....	..
3	Drying at 65° C.	..	..	..	..	Bad	Bad
	Drying at 30° C.	..	..	..	..	Bad	Good
	Plasticity	..	..	..	..	Good	Fair
4	Drying at 65° C.	..	..	..	..	Bad	..
	Drying at 30° C.	..	..	..	..	Bad	..
	Plasticity	..	..	..	..	Good	None
5	Drying at 65° C.	..	..	..	Bad	Improved	..
	Drying at 30° C.	..	..	..	Bad	Good	..
	Plasticity	..	..	..	Good	Fair	None
6	Drying at 65° C.	..	Bad	..	..	.....	..
	Drying at 30° C.	..	Bad	..	..	.....	..
	Plasticity	..	Good	None	..	.....	..

1. Dark gray massive clay, underlying a lignite seam, Estevan, Sask.

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2. Light gray massive clay, Coleridge, Alta.

3. Dark gray soft shale, underlying a lignite seam, Tofield, Alta.

4. Light gray hard shale, overlying coal seam, Old Man River, Alta.

5. Soft olive shale, Gwynne, Alta.

6. Soft shales interbedded with streaks of sands, Camrose, Alta.

The clays were heated in a small rotary drum, made of sheet iron and having baffles projecting from the inside to keep the clay well stirred up and evenly heated.

A stationery sheet iron hood enveloped the drum, except where openings were left for the gas flames to enter. The drum, which was revolved by hand, was provided with a hollow axle, through which a pyrometer tube was inserted. About one-half to three-quarters of an hour was generally taken to bring the clay to the required temperature, the latter being easily kept constant during the time allotted for treatment.

The length of time allowed at each temperature was fifteen minutes, each clay being kept for this period at successively higher temperatures until it yielded to the treatment. Other trials were made of thirty minutes' duration at certain temperatures, to show the effect of time. The latter results show that it is possible to obtain effects at lower temperatures with increased time similar to those given in the shorter time at higher temperatures; but this appears to be true only within certain limits, for Professor Orton's experiments show that these clays were not improved by exposure for one and a half hours to a temperature of 400° C.

Steam was given off freely from the heated clay at all temperatures up to 500° C. The fumes evolved at higher temperatures smelled strongly of sulphur and hydrocarbons, which were probably due to the dissociation of particles of pyrite and driving off of bituminous matter. When the heating was completed all the clays except No. 2 were much darker in color than in the raw state, being dark gray to almost black. The results are tabulated in Table II.

Clay No. 2 yielded at a comparatively low degree of heat

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treatment, probably due to its containing a greater amount of grains larger than clay substance than any other of the samples tested.

The tenacity with which clay No. 3 clings to its plasticity under the action of heat is remarkable, since that property was not affected to any great extent even at the highest limits of the experiment. It would, no doubt, succumb to a more prolonged exposure at 550°, or it might be successfully treated at 600° for fifteen minutes. The latter was not tried, however, for it was possible that the amount of preliminary heating that could be economically applied in practice to this or similar clays was already exceeded.

The results given by sample 4 show the slight margin in time that exists between the proper and unsuccessful handling of some clays. After the thirty-minute treatment at 550°, this clay was sandy in texture and could not be molded into shape, while after the fifteen-minute treatment its defective qualities were quite unimpaired. The precise time, then, for the clay at this temperature appears to be either twenty or twenty-five minutes, but, as will be explained later, the thirty-minute treatment was not fatal.

The results of previous experience without any special apparatus showed that the clays would require a high degree of heat treatment, but to avoid mistakes all the clays were heated to 350° C.; however, since no change occurred in any sample at this temperature it is unnecessary to include it in the table.

The test pieces made up for the drying tests were 2^1_2 inch cubes, since there was not a sufficient quantity of the various clays in stock to make full sized bricks. The cube, however, has a greater volume for the amount of surface than any of the brick shapes.

The dryers used in the experiment consisted of small chambers attached to the steam-heating apparatus of the building. The maximum temperature that could be obtained in this way was about 65° C., the pieces being dried in from 24 to 36 hours. Although faster dryers are used for some clays in practice, it was decided that, if the clays can be worked and afterwards

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dried safely at the above temperature, the object of the experiments had been attained.

The preheating treatment causes marked changes in the character of the clay, the most important for practical purposes being the change from a tough sticky mass, having undue shrinkage and abnormal cracking in drying, to an open granular body that can be easily worked and rapidly dried.

The effects obtained by preheating to the above temperatures are not permanent. The plasticity of the clays No. 4 and 6, apparently destroyed during the course of the experiments, was restored again by allowing these clays to remain in an excess of water for 24 hours. Sufficient water was then evaporated so that the clay could be remolded and set to dry. No. 4 would still stand fast drying, but No. 6 cracked both in the fast and slow dryer. Again when the cubes made from No. 6 were dried, reground, and wetted for the third time, it was found that this clay had regained all its former plasticity and stickiness; small bricklets then made from it cracked while air drying at room temperature quite as badly as the raw clay did.

Clay No. 1 undergoes a slight preheating through a rotary dryer in the brickworks at Estevan. This is done primarily to prepare the clay for dry-pressing by getting rid of the superfluous moisture which it contains in the bank; but the treatment was also found to stop much of the fire checking to which the raw clay was liable. The losses from fire checking are still great, but a higher degree of heat treatment would probably do away with it entirely. It is doubtful if the kind of apparatus in use at Estevan would give a sufficiently high temperature to drive off combined water and render the clay fit for wet molding processes.

THE EFFECT OF BENTONITE.

About 20 feet below the beds from which sample No. 6 was taken, a seam about two feet in thickness of the clay known as *bentonite* occurs. This variety of clay is of yellow color when fresh from the bank, but assumes a dirty white color on exposure. It is fine in texture, exceedingly smooth, and forms a very soft soapy mass when mixed with an excess of water. It has an extraordinary capacity for absorbing moisture, being capable

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of taking up three times its weight in water. The clay possesses marked detergent properties and was used in the early days of the Northwest by Indians and Hudson Bay Co. employees as a substitute for soap.

This material was rejected as unfit for any burned clay wares, but an attempt was made to dry in a moist atmosphere some bricklets made from it. After three weeks of gradual drying the bricklets showed abnormal cracking and very high shrinkage. Although none were observed on the outc op, it is possible that some thin streaks of bentonite were included in the beds sampled for No. 6. Certain of the sand beds of the vicinity were found to possess plasticity, and some decidedly silty beds will crack in slow drying.

As a good deal of the material which composes these beds is derived from the erosion of the lower Cretaceous, which contains bentonite beds, it may be assumed that this material, being part of the product of erosion, was redeposited and distributed through many of the later beds.

It occurred to the writer that some simple scheme of washing might be adopted to separate the pasty constituent from these clays. As an experiment, one pound of ground shale from sample No. 4 was well stirred up in about a gallon of water and allowed to settle for two hours, the water and suspended matter being then drawn off. This operation was repeated, and the residue allowed to dry. When the residue had dried, it was found to consist of a badly cracked yellow paste about half an inch in thickness, forming a crust on top of dark gray sand and silt. The yellow paste had all the appearance and characteristics of bentonite or soap clay.

The shale when dry was found to have lost 25 per cent. of its weight, presumably all of it being pasty matter held in suspension and drawn off with the water. The plasticity of the shale was much reduced by the washing, but it cracked almost as badly as ever in the 65° dryer. It would dry intact though in room temperature.

That the presence of bentonite is a potent factor in producing air cracks was proved by the following experiment: ten per cent. of bentonite from Camrose was added to a coarsely ground

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paving brick shale from Elmira, N. Y. The cube made from this mixture cracked badly in the 65° dryer. The Elmira shale will stand fast drying at 85° C.

Between bentonite as an extreme case and clay No. 2 as a mild example, we have clays containing varying amounts of gelatinous paste which allows the water to escape with difficulty from the body, and causes cracking while retarding drying.

The chemical analysis of bentonite (see Table I) showed that it possessed a large amount of hydrous silica, which probably causes that sticky type of plasticity and the trouble in drying.

Preheating has the effect of driving out the water from the hydrous silica, and causing the caking together of the dehydrated particles which gives the granular texture seen in the clays thus treated.

Clay No. 3 was washed in a similar way to No. 4, but lost 75 per cent. of its weight and the residue cracked in drying. The chemical analysis made of it shows only a small amount of hydrous silica; but this clay, notwithstanding the low amount of that ingredient, possesses all the pastiness of bentonite, and its tendency to crack is almost as pronounced.

A large percentage of this clay is in a very finely divided state, and much of it may be colloidal matter; perhaps organic colloids are also present. Then in this case, preheating to sufficient temperatures has the effect of driving the water from the infinitesimal pore spaces between the minute grains, and the chemically combined water from the colloids. The minute particles when deprived of their water envelope appear to adhere in sufficient numbers to form sizable grains.

The subsequent safe drying after preheating seems to depend on the fact that the water with which the clay was tempered escapes by evaporation in the dryers before it has time to permeate the microscopic pores again and hydrate the colloid or siliceous content.

Clays which retain or regain their plasticity after the expulsion of chemically combined water have been recorded at various times. H. E. Kramm[3] found that test pieces made

[3] Trans. A. C. S., Vol. XIII, p. 698.

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from mixtures of kaolin and gypsum, kept for 8 hours at a temperature of 790° C., slaked down in water and had lost little or none of their original plasticity.

CONCLUSIONS.

Most of the clays can be made workable by the preheating process if commercial conditions allow of its use. This process involves the use of a suitable type of rotary kiln, a cheap fuel to supply the high temperatures at which these clays must be treated, a proper superintendence in controlling the process, and the cost of extra labor. The samples on which the experiments were made have been selected from localities in which either coal, lignite or natural gas are abundant.

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THE MANUFACTURE OF PROMENADE TILE.

By GEORGE W. SHOEMAKER, Columbus, O.

INTRODUCTION.

Definition of the Term.—The name *promenade tile* seems to be an Americanized trade name for *English quarry tile.* They are practically the same, both being apparently made by the stiff mud process, but the foreign tile are repressed and the American tile are not. There may be a very few promenade tile manufactured in this country that are repressed. The market value is some in favor of the foreign tile, although, if quality speaks for market value, the highest quality of American promenade tile has no superior.

Classification.—Before taking up the manufacture of promenade tile, let us put them in their proper class among clay products. Their uses, which are two-fold, namely, for flooring and roofing, will to some extent govern their classification. As a flooring material, they might well rank next to the highest grades of flooring tile, although very much cheaper in price. Their excellent qualities have been proven by the variety of uses to which they have been put. These show their durability and value as a flooring material. A little observation will soon reveal their coming popularity from their use in the higher classes of architecture such as depots, roof gardens, theatres, hotels, banks, libraries, administration buildings, drug and department stores, creameries, laboratories, hearths for mantles, and, in fact, anywhere that the higher grades of flooring tile are used. As a roofing material, they can be used for coverings of flat or very low-pitched roofs only. Their ability to withstand everlastingly climatic conditions places them in the highest rank beside roofing tile, which are used on roofs of steeper pitch. In fact, promenade tile are sometimes called roof-plates to convey the idea that they can be used for a roofing tile.

Description.—Promenade tile are generally larger in size than the higher grades of flooring tile and either square or oblong. The most common sizes are $3'' \times 3''$, $4\frac{1}{2}'' \times 4''\frac{1}{2}$, $6'' \times 6''$, $6'' \times 9''$, $9'' \times 9''$, and $12'' \times 12''$ surface area, and from $\frac{3}{4}''$ to $2''$ in thickness. The under side of the tile is generally corru-

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gated; and when the corrugating is properly done, it will give greater adhesion to the cement bed in which the tile are laid than the higher grade of flooring tile. The common colors are the varying shades of red, although chocolate, black, flashed effects, buffs and grays, can be made.

MANUFACTURE.

CHOICE OF A CLAY.—PROPERTIES OF THE BURNED CLAY.

In taking up the manufacture of promenade tile of the highest quality made by the stiff mud process, some essential and vital points must first be considered and proven in regard to the adaptability after burning of the clay or shale for this kind of product. These are: color, structural density, toughness, freedom from warpage, hardness, smoothness of surface, and freedom from flaws.

Color.—The first point to decide in selecting a clay or shale for the manufacture of a promenade tile is the color it will produce when burned hard enough for marketing. This should be proven absolutely satisfactory, for a poor color will reduce the value of the product as much or more than some other defects. In a case of competitive selling, the market will usually select the tile of richest color, if at the expense of minor defects. In the majority of cases, the market will demand solid colors, although polychrome effects are not unusual and they give surprising beauty. Flashed shale tile generally give polychrome effects.

Structural Density and Toughness.—Tile of this character have the greatest of structural density to insure life against abrasion and also to prevent the absorption of dirt.

There are several reasons why toughness is desired. The rough usage they undergo in kiln drawing, stock piling, loading in cars, transportation and delivery from cars to destination, and sometimes the unusually severe use they are compelled to withstand, show in a way the hardships they must undergo and yet retain their nicety. If this particular property of toughness is lacking, the trade will soon remind us of "recharges" for broken, cracked, or chipped, tile.

Other Properties.—The face of the tile should be practically

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level, although if slightly sunken in the face, they can be laid without much notice of this defect. They should be harder than steel in order to easily resist the constant scratching from shoe nails. The surface should have a smooth compact texture; and the face and edges should be free from cracks, blisters, unintended marks, and discolorations. Internal flaws, such as cracks, bloating, and air checks, should also be absent. The variation of lengths or widths should not be over $^1/_8''$. In a variation of colors or a polychrome effect, this variation in lengths and widths might be as great as $^1/_4''$. The edges should be sharp and well defined, and the ends, where cut at the cutting machine, should be smooth and square with the sides.

CHOICE OF A CLAY.—PROPERTIES OF THE RAW CLAY.

When a clay or shale has proven itself worthy in the above respects, then its physical and mineralogical properties should be investigated in every step of the process of manufacture. These properties, of which there are many, are of no small consequence. One alone may be the cause of failure to manufacture a high-grade product.

The surest way to reach a conclusion in regard to the adaptability of a clay or shales for the manufacture of this class of material is first to classify the essential and ideal properties that a body should have throughout the process of manufacture. Some properties are essential to the highest degree, while others can be greatly modified from the ideal and yet prove quite worthy.

Ideal Properties.—A clay or shale of ideal physical properties for this purpose should be:

Easily ground to the desired fineness.
Easily screened to the desired fineness.
Quick to slake with water in tempering.
Easily pugged to a homogeneous, doughy state.
Plastic to a point of safety with other properties considered.
Of high binding power.
Easily forced through a die without lamination or cracking.
Free from warping and cracking in drying and burning.
One having greater shrinkage in drying than in burning.
One having physical properties safe under fast burning and cooling.

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A clay or shale of ideal mineralogical properties would be:
Free from efflorescing salts.
Free from pyrites, and other compounds of sulphur.
Free from fibrous and solid carbonaceous matter.
One containing no calcium carbonate or a very small amount in a thoroughly disseminated state.
One containing a certain amount of free silica to take care of unusual shrinkage in burning.
Not too fine or too coarse in grain.

A clay or shale can have the very best of physical properties, and its mineralogical properties can be of such character as to give a worthless product or the reverse case.

The ease with which a clay or shale can be finely ground and screened is of much importance. It decides to a great extent the line-up of machinery used for these purposes and also figures in the power and labor cost in this step of the preparation. It may have such characteristics as to hamper the output much below profitable manufacture, unless machines of greater grinding and screening capacity are used. In this we reach a limit, unless a greater number of machines are used, and then the cost of manufacture increases in proportion.

The readiness of a clay or shale to slake easily with water in tempering and pugging to form a homogeneous, doughy mass, generally shows its importance in the process of manufacture.

If obstinate in this respect, it is usually a source of die trouble and dryer cracking, moreover, the surface of the tile after burned will generally be much rougher than if the body had been homogeneously pugged.

A certain amount of plasticity is much desired; but if in the extreme either way, disaster generally follows.

Some clays and shales require a greater amount of water than others do in the tempering and pugging to bring out the desired amount of plasticity. If we can use a small amount of water to bring about the desired plasticity, we will to some extent keep away from die trouble, dryer cracking, and warping.

High bonding power is much desired for several reasons. In forming, if the body has a good bond, the column both at die and cutting machine will need less attention. In placing the

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wet tile on palettes it reduces the chances of breaking in handling; and also less care need be exercised in kiln setting, which will reduce the cost of this item.

The closer the properties of the clay or shale are to the essential and ideal, the cheaper will be the cost of manufacture through the various steps where they will show their ill effects. It would be a difficult task to find a clay or shale that would not show some undesirable properties. The principal point sought is the correction of the ill effects of the undesirable properties to a point of safety in manufacture.

PREPARATION OF BODY.

Blending.—One of the most important factors in the preparation of a clay or shale is to have a thorough mixture of the various strata of clay or shale that are to be used. If it is not practical to do the blending at the mine, some provision should be made at the grinding station in order that this can be done with the greatest accuracy. It can be done conveniently at the pulverizer or dry pan if a proper separation of the clay or shale strata has been made so that they can be easily assembled and conveyed to the grinding machines.

Grinding.—In the ordinary process of preparation, if the clay or shale is of such character that a pulverizer is not needed, the body is ground through a dry pan that has screen plates with $^1/_{16}$″ to $^1/_4$″ openings. If the clay screen is of a fine mesh, the openings in the dry pan screen plates should be smaller. There is a small saving in power cost by not lifting this coarser ground material to the clay screen; it tends to lessen also the cost of up-keep of the screening machinery. The one most essential point in this connection is that if we have in our mixture of clays or shales from different strata one of a very soft easily powdered type and another from a hard rock-like formation and attempt uniform blending in the grinding with the openings on the dry pan screen plates much larger than those of the clay screen, we may have trouble from separation of these strata. We will find at intervals the proportion of the easily powdered type running to the screen much higher than desired; moreover, the grinding machinery will become overcrowded with the harder type; and, naturally, feeding must cease until the dry pan cleans

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itself. This plainly shows that the mixture is not in the proportion expected. The properties of two clays may be quite opposite, one a fine grained plastic type and the other a coarse grained sandy type, and by the hit and miss mixture, untold trouble may be caused at the die, in drying, in burning, or in the quality of the tile after burning. It is of much importance to learn the widest limit of variation of proportions permissible in the blending that will give satisfactory results, then to arrange to hold the blended mixture within the proper limits.

Screening.—After the ground material has passed through the dry pan, it is lifted, most generally by a bucket elevator, or conveyed to the clay screen, which is usually some standard type. The clay screen should not be coarser than 18-mesh, and many clays or shales will require finer screening than this to produce the desired texture in the body.

Pugging.—The screened material then passes to a storage bin or directly to the tempering and pugging machinery. Some manufacturers use a wet pan and granulator, while others use some standard type of pug mill. The length of time required for pugging depends on the amount of plasticity in the body and the amount needed further for purposes of manufacture.

FORMING.

The Auger Machine.—The pugged mass is then either conveyed to a soaking pit for aging a certain length of time before using or is used direct in the auger machine. The auger machine used for this purpose should be able to withstand considerable strain, for the aperture of the dye is quite small and much pressure is used to force the tile column through it.

Dies.—There are three types of dies:

The four-tile die, which makes four tile at a single cutting.

The double-tile die, which makes two tile at a single cutting.

The single-tile die, which makes one tile at a single cutting.

The four-tile die is practically a hollow building-block die with knives in the corners to slit the sides about one-half to two-thirds of its thickness, so that after burning the tile box can be broken apart into four-tile. This type of die never produces a tile of the highest quality. The knife marks on one side of each tile

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generally mar it. The face of the tile is the outside of the box, and the face of the under tile is always spoiled at the cutting machine by the cutting wire going through the back side of the tile first and chipping or flaking off small pieces of the face, thus leaving a ragged edge. There is great danger of the faces being finger printed in hacking; and by setting these tile boxes on end on the palettes, more or less of them are badly bruised. There are numerous other circumstances that tend to lower the quality of the tile made by this type of die. Not over seventy-five per cent. of the tile can be first-class.

Next is the double die, which makes two-tile at each cutting. Tile made from this type of die are generally of higher quality than those made from the four-tile die, although only one-half of the tile made from this die can be expected to be first-class. The face of the under tile is marred in passing over the rolls of the cutting machine. The cutting wire, passing through the back side, flakes pieces off the face and also leaves a very ragged edge, just the same as on the bottom tile from the four-tile die. The tile are also generally belt and palette marked. By this method of forming, we knowingly can figure not more than fifty per cent. as of first-class, although, as stated above, the tile are in quality above those made by the four-tile die method.

If a tile of the highest quality is expected and the cost of manufacture has been considered, why should we select a type of die that we know will make from twenty-five to fifty per cent. of second-grade tile from no other cause than the die? There are really no great advantages over the single die gained by the above types to invite their use. The capacity in pieces of an auger machine is about the same for the three types. The general manufacturing cost of a tile made by the single-die is slightly above the other two; but every tile made by a single die and placed on a car for the dryer has a chance of being first grade. This is not so with the other two types of die. Single dies are cheaper and after being used a while can be redressed and used again. Some clays might require lubrication; but some of the highest quality tile in the market to-day are made over a dry die. The up-keep of a single die is very low, and the die requires slight attention during the operation of the machine.

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Cutting-Tables.—When the body reaches the auger machine it should be in its proper state to be issued through the die in its proper form. This form will be a ribbon-like column which passes over the cutting-table and is cut into the proper lengths. The type of cutting-table used for this purpose is quite similar to the standard makes of drain tile cutters.

DRYING.

Palettes.—The tile are lifted one at a time from the off-bearing belt and placed upon wooden palettes, which are then set upon the drying car.

The palette should be flat open slat work, practically level, and very strong. The size of the surface is governed by the size of the tile and the number we wish to put upon them. The palettes should be of such measurements that no car space is lost.

Dryer Cars.—The cars used are of special design. One object in using a special type car rather than the ordinary brick dryer car is capacity. A car best suited for the purpose is one that will hold from 500 to 700 tile of the $6'' \times 9'' \times 1''$ size, with sufficient air space around the tile for proper drying. The type most generally used have three or four upright standards; these are divided into ten or twelve spaces by cross arms, upon which are placed wooden slats or angle irons to hold the palettes.

The Dryer.—There are no special features needed in a dryer for drying promenade tile. Almost any of the modern brick dryers that can be regulated to practically constant temperatures in the hot end and that have proper circulation can be used.

The cool end of the dryer should not be kept at a temperature much over 100° F. This allows the tile in the wet state to temper somewhat before being subjected to the higher temperatures. The danger point of cracking and warping in drying seems to be between the time the ware enters the dryer in the wet state and the time it reaches leather hardness throughout; although if the cracking once begins in the wet state, it may continue to increase until the tile is perfectly dry.

Setting.—In setting these tile in kilns for burning, experience teaches the use of boxes made of flat fire clay slabs. These boxes in which the tile are set are built up of these slabs as the set-

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ting proceeds; they resemble somewhat a saggar setting effect except that both ends are open. The tile are laid flat and piled in stacks of from 10 to 20 tile per stack, the number of stacks in a box being regulated by the size of the tile and the size of the box bottom.

Kilns.—The types of kilns most generally used are the round or square downdraft. These are about equal for their good and bad qualities.

Fuels.—The different kinds of fuel used for burning are coal, gas, and crude oil. Gas, as a fuel for this purpose, is usually some higher in price than other fuels; but when the higher quality of the burned product is taken into consideration, its use is often quite economical. Some of the advantages over coal gained by burning with gas are: brighter and richer colors and shades, more uniform shades, less per cent. of off-shades.

The Burning Proper.—The general features of the burning are practically the same as in burning a red shale, stiff-mud brick. The time required for burning should be much less than with brick, owing to the smaller tonnage of clay mass, the small size of the sections, and the weight of each section being independent of any other section. The openness of setting also allows greater speed in burning. It must be understood that in the burning of these tile, they undergo the same dangers as in the burning of red shale, stiff-mud brick, but in a shorter period of time.

Cooling and Drawing.—It is quite worthy of mention that care should be exercised in cooling a kiln of promenade tile to keep cold air currents from circulating in the heated kiln, for air checking is sure to follow. This air checking in tile is of more serious consequence to the tile maker than air checking is to the brick maker. A promenade tile, owing to its uses, when once air checked is a practically worthless product without a market value, while an air checked brick, if the defect is not of too serious a nature, has a market value equal to that of a common brick or higher. In emptying or drawing a kiln of tile, the same method is used as in brick or roofing manufacture, that is, by barrows or conveyors.

Sorting and Shipping.—The tile are taken from the kiln to the various stock piles to be shaded and graded into various

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classes. They are generally shipped as car lots, being loaded in the cars quite like face brick, although the ends should be strawed and two wooden laths used between each course to prevent the sides from rubbing and chipping in transportation. The average car load is generally ten thousand. Small lots are generally shipped in barrels or crates.

DISCUSSION.

Mr. Richardson: I would like to ask Mr. Shoemaker a question. Where are you manufacturing tile as described in your paper?

Mr. Shoemaker: We have a factory at Lexington and another in Pennsylvania.

Mr. Gorsline: I wish to say in regard to the use of the words *promenade* and *quarry* that *quarry* means square. In Wales, the home of the industry, it is applied only to square tile and should not be applied to $6'' \times 9''$ tile, which latter are in this country now accepted as *promenade* tile.

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THE INFLUENCE OF THE COMPOSITION OF THE STAIN IN THE PRODUCTION OF RED FROM CHROME-TIN PINK STAINS.[1]

By Ross C. Purdy, Columbus, O.

INTRODUCTION.

Having found that nearly every writer on this subject, since the time of Seger, has repeated statements that were not in keeping with factory observations, the present writer was prompted to make extensive investigations to determine whether these statements were true or were mere repetitions. The first of these investigations was reported to this Society by Purdy and Brown[2] and the second one was reported by Rea.[3] The present report is the third one of this series. Further investigation is in progress.

Mellor[4] criticized the first of this series of investigations, making false assumptions concerning our experience and methods. Using the phrase "arrested reactions," he asserted that a cone 5 calcination in 12 hours without washing and recalcination was impractical and that our results differed from what he found because in his work he approached nearer to practical conditions and completed reactions. He assumed, further, that we calcined our stains under reducing conditions.

We have the following facts on our side of this question:

(1) Our first calcination (cone 5) was made under no less severe heat treatment than was our practice in the factory. Under factory conditions, I have made 200-pound batches of chrome-tin pink stains, calcining them at cones 2 or 4, and using them directly from the saggars without washing or recalcining. In this manner we obtained a stain which gave as beautiful a blood-red glaze as I have ever seen produced with chrome-tin.

(2) Not much of a deviation could be made from the proportions or kinds of materials used in this stain without changing the tint obtained, notwithstanding the fact that our glaze was the same at all times.

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[1] Contribution from the Ceramic Engineering Laboratories of the Ohio State University.

[2] Transactions, Amer. Cer. Soc., Vol. XI, p. 228.

[3] Ibid., Vol. XII, p. 518.

[4] Trans. English Cer. Soc., Vol. IX, p. 89.

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(3) The empirical molecular formula of this stain could be given away with full confidence that the exact tint we obtained could be duplicated only by the use of the same materials that we employed.

(4) Those stains, calcined at cone 5, which had the same formula and materials as the stain given by Seger gave the same brownish tints which Seger's stain has always given under every condition tried.

(5) The kiln we used is *not* a small, bench gas muffle. Its inside dimensions are $12 \times 13 \times 26$ inches. The gas flames pass from a commingling flue below, through tubes up the sides of the muffle, to a common flue above the muffle. Each of the four gas burners has a good air mixing attachment. With this kiln we can obtain a more continuously oxidizing condition than is possible in any of our solid fuel kilns. We certainly burned our stains under most excellent oxidizing conditions.

(6) Mellor cannot deny the absurdity of discussing completed reactions in such stains as this, which, as he admits, are nothing but lakes.

(7) We obtained most excellent red glazes in that first experiment with unwashed, cone 5 calcines.

(8) We reserved judgment on the effect of higher calcining treatment and of washing and recalcining. Our first study, as was plainly stated, concerned only the results obtainable with unwashed stains, once calcined at cone 5.

I do not hesitate to repeat, therefore, the claims made in our first study and to which Mellor took exception.

(1) "At the present stage of these investigations, it appears to be a case of an exception, rather than a rule, for stains of like empirical molecular formula, but different chromium source to coincide in their resultant color productions."[1]

(2) Much stress has been laid upon the idea that composition of the glaze is more important than the composition of the chromium-tin pink stain. Quite the reverse of this would, in light of the present investigation, seem to be true. It must be granted that the glaze must be relatively low in lead and alkalies

[1] Loc. cit., p. 253.

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and high in calcium. Beyond these limitations, however, there seems to be very little, if any, that is requisite.[1]

THE PRESENT INVESTIGATION.

The present investigation of this series was to determine the effect of (1) calcining under more severe heat treatment, and (2) of washing. For this study, those stains, described by Purdy and Brown, which have odd numbers were used. The history of these stains is: (1) calcined at cone 5 in 12 hours, (2) remixed, (3) calcined at cone 8 in 26 hours, each stain divided into equal portions, one of which was thoroughly washed and recalcined at cone 8 in about 20 hours, all the calcinations being made under oxidizing conditions.

The glaze used and the glost heat treatment were the same as in the former studies.

The Trials and Manner of Setting.—Two sets of trials were prepared, one set consisting of tiles and the other of individual butter plates.

The tiles (wall tile biscuit) were placed on setters, six setters to a saggar, so that all the tile in a given saggar were alike subjected to whatever chromium fumes may have been present. In every instance there was enough of chromium fumes to make the clear glaze-wash on the inside of the saggar turn to a dark green. The burning of this set of trials was made under oxidizing conditions with coke as fuel.

The small butters were placed in pairs, one inverted on its mate, and the two sealed with a plastic porcelain body mixture. These sealed butters were then piled in small bungs in glazed saggars that had not been subjected to chromium fumes. This scheme was resorted to so that each glaze should be in an atmosphere of the same sort, and degree of concentration, of chromium fumes as it would have been in a saggar set full of ware of only the one glaze. This burn also was oxidizing.

We have, then, two sets of these glaze trials, one in which all the glazes were subjected to chromium fumes sufficiently strong to color the sides of the saggars dark green and the other in which each individual glaze was so sealed within the inverted butters

[1] Loc. cit., p. 255.

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as not to permit the escape of enough fumes to even tint the glazed sides of the saggars. In the first set of trials ample opportunity was given for equalizing the differences caused by (1) the quantity and (2) the source of the chromium, and in the second set no such opportunity could have existed.

RESULTS.

Effect of Chrome Fumes.—No difference in depth or character of tint was obtained in the corresponding glazes of these two sets of trials. The chromium fumes to which the first set was subjected did not tend to equalize the tints produced.

Tints Obtained.—The tints obtained were substantially the same as those described by Rea,[1] the differences being only such as would have been expected from the differences in composition.[2]

Effect of Washing and Recalcining.—No effect of this treatment can be discerned. No one could discern any differences in the corresponding glazes of the washed and unwashed stain series of either sets of these trials.

Effect of Increased Calcining Heat Treatment.—There is no marked difference between the tints obtained with stains calcined first at cone 4 and then again at cone 8, and those which were twice calcined at cone 4. We believe with the other writers on this subject that it is best to calcine the stains at as high a temperature as possible and for as long a time as possible. In fact we know this extremely high heat treatment of the stain is essential for stains used in high fire glazes. This phase of the subject is now being studied by one of our students.

Effect of Difference in Source of the Chromium.—I can say now, as in the beginning, that the use of different sources of the chromium in the stain will produce different tints and in some cases, such as lead chromate as compared with $K_2Cr_2O_7$ and Cr_2O_3, different colors.

Importance of Stain Composition.—The same differences, wrought by the different amounts of CaO in these stains, can be seen in these cone 4 + cone 8 trials, as were noted in the cone 4 +

[1] Loc. cit., p. 525, 526, 527.

[2] Rea used the even numbers while here the odd numbers were used.

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cone 4 trials. In this respect, our results are rather surprising. The difference between the brownish pinks and brownish reds of the high CaO stains and the lilac pinks and reds of the low CaO stains was not as great as we had expected or near as great as the other writers in this subject would lead one to believe. The pure pinks and reds were obtained only with the equivalents of CaO 2.0 and 1.5 in the stain.

With increase in chromium in the Cr_2O_3 and $K_2Cr_2O_7$ stain glazes, the tints pass from pink to red and then to green, while in the lead chromate glazes the tints pass from pinks to brown reds.

The best reds were obtained with $K_2Cr_2O_7$ and the darkest pure red with Cr_2O_3 and lead chromate.

CONCLUSIONS.

In conclusion, I must say that while some slight differences in tints were wrought by the higher calcining heat treatments (as they were expected by us), we can re-affirm our belief in the following:

(1) Composition of the stain is as vital as the composition of the glaze.[1]

(2) Difference in source of the chromium makes a difference in the tint obtained.

(3) Not all, if any, of these stains need to be washed or recalcined.

(4) It is best to calcine the stain at as high a temperature as possible.

DISCUSSION.

Mr. Mayer There are some points Professor Purdy has brought out that do not agree with my experience. This question of the manufacture of underglaze pink for printing and lining has so many aspects that are so scantily touched on in the literature of the subject that it is very difficult in a discussion like this to say all one wants to and attempt to cover the ground properly. What I mean exactly is this, given a pink color that can be successfully used under a given glaze and which will in a

[1] This would have been better shown in the more complicated mixtures which I used commercially.

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certain place in the kiln come out all right, the same pink in a hotter part of the kiln may be, and probably will be, utterly ruined. I use a pink that at cone 3 is good—very good pink—and at cone 4 it is ruined. Again, a pink may be perfectly good under a normal thickness of glaze, while it is entirely destroyed when the coat is too heavy.

The presence of calcium oxide in the glaze, amounting to at least 0.5 equivalent in the RO of the formula, has appeared to me to be a necessity to keep the color good at cone 3. By increasing the calcium oxide above this limit you can make a glaze that will make the color stand much more fire than cone 3; but I must add that I could not make a glaze that would not scum when I increased the calcium over 0.5 equivalent in the RO of the formula.

Working on a suggestion made by Mr. A. S. Watts, I found I could take a pink color that under the usual treatment, *viz.*, firing with plenty of air and with the color spread thin, say not to exceed ½″ thick, was very liable to be destroyed at cone 1 or less, and by treating in the manner he described, I could make it stand at least two cones higher heat. The treatment I have adopted is as follows: The pink color mixture is thoroughly mixed either two or three times through a sieve or better on a ball mill and then dried. It is then made up into balls—using a little dextrine in the water—not exceeding $^{5}/_{8}$″ diameter and fired with plenty of air in a biscuit firebung. This operation is repeated three times, care being taken to grind and wash after each firing.

Since adopting this method of preparing the pink color, I have had no more loss with this color than with any we make, and in most cases the method of preparation makes the difference between success and failure.

I may add that when treated this way the composition of the color—inside of reasonable limits—does not cut a serious figure in the results. I have taken colors treated in the old method that I had in stock and could not use and refired them in the way described; they have turned out perfectly satisfactory.

Glazes high in alumina destroy pink color. This I found from making a very extensive series of experiments with a view

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of stopping the solvent action of the glaze, and, very much to my surprise, the more alumina I added the worse the color got. My experiments showed also that with what would under normal conditions be considered an excess of lead the pink color was not affected. This latter experiment would appear to indicate that the solvent action of the glaze when excessive is not detrimental to this color.

I ought to state that as the heat of the European pottery kiln is so much below our heat, this pink color presents little or no difficulty to them.

Prof. Purdy: In this study we had a change in the tint and a change in the depth and character of the color with practically slight change in the composition of the stain, using the same glazes. We got a change in the character of the color produced with these changes in the stain in this one glaze that was as marked as any change I have seen with a change in the glaze. I have had the same experience Mr. Mayer has had where some glazes would destroy the color completely, but that does not destroy the fact that while you can use a large variety of glazes you cannot have a very large variety of stains and yet produce a good pink.

Mr. Mayer: There has been a great deal said about the variation in the color. There is a great deal of variation in the color depending on how it is put on. Using the same color, you will get some very light pinks and very dark maroons. The question of the variation is very largely a matter of how the article is manufactured.

NOTE WRITTEN AFTER READING THE ABOVE DISCUSSION.

Mr. Purdy: Mr. Mayer has dwelt much on the influence of methods of preparation and use, and on factors other than composition of the stains. His remarks on these are very true to the facts.

After reading the discussion by Mr. Mayer and a paper by C. E. Ramsden,[1] it appears that the reason for our difference in experience regarding the relative importance of composition of the stain, the source of the chromium, and the methods of

[1] Trans. English Cer. Soc., Volume XI, page 29.

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preparation, is that all of these gentlemen from Dr. Seger down were and are talking about under-glaze print colors while I have been talking about colored glazes, *i. e.*, glaze in which the chrome-tin pink is suspended and partially dissolved as a colorant: For under-glaze work these stains must not be at all dissolved by the glaze, for if they should be, the print would run, while on the other hand, as glaze stains they must be thoroughly disseminated and partially dissolved. These two cases therefore are radically different, and one cannot argue from the one to the other concerning the relative importance of any of the factors involved. It stands to reason, however, that in under-glaze prints, the composition of the glaze is of more importance than in the case of glazes colored by chrome-tin pink. For colored glazes, I still maintain that the composition of the stain and the source of the chromium are of as vital importance as the composition of the glaze.

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A COMPARISON BETWEEN THE RATTLER TEST AND THE SANDBLAST TEST FOR PAVING BRICKS.[1]

By EDWARD ORTON, JR., Ohio State University.

At the summer meeting of the American Society of Testing Materials, held at Atlantic City, June, 1909, the subject of a better standard test for paving brick was taken up in Committee C. 3 and discussed at some length. The writer was not present at the meeting, but was informed that the rattler test received a somewhat severe scoring at the hands of some members of the committee, and that as a substitute test the use of the sandblast was suggested by Mr. L. W. Page, of the Road Materials Laboratory at Washington. The writer is not informed just how much stress was laid upon the suggestion, or whether data was submitted in support of the same, since the deliberations of the committee were not transmitted to the Society or otherwise published. Some work along the line of testing the wearing quality of paving bricks has, undoubtedly, been done at Washington under Mr. Page's direction, for test pieces upon which the blast had been applied have been seen and examined by various persons.

The suggested use of this method made it seem worth while to learn what its merits really were. As the writer was at that time making a study of paving bricks for the Geological Survey of Ohio and had an extended series of rattler tests to make, it was thought that if the sandblast test could also be applied to the same set of samples, it would give exactly the kind of comparison which would be most valuable.

The Bureau of Standards, at their Pittsburgh laboratory in 1910, installed a sandblast machine for testing work of various sorts. Application being made in May, 1911, to the Director, Dr. S. W. Stratton, to be allowed to use this machine for the proposed series of tests, permission was promptly and willingly granted. The writer takes this opportunity to return thanks publicly to Dr. Stratton and to Mr. G. H. Brown, who was in immediate charge of the ceramic equipment at Pittsburgh at that time, for their kind coöperation and assistance.

[1] Published in advance, by permission of J. A. Bownocker, State Geologist of Ohio.

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THE BUREAU OF STANDARDS SANDBLAST EQUIPMENT.

The sandblast injector was purchased ready for use from a number on the market. It was made by J. M. Betton, 178 Washington Street, New York, and is known as the Drucklieb Injector Sandblast Apparatus. The cross section of the machine, taken from the descriptive circular, is shown in Fig. 1.

The Sand Valve and Injector.—One alteration of the apparatus had been found necessary by Mr. Brown, *viz.*, the sand valve was unsatisfactory, giving an unequal flow of sand at different points of its circumference, and he had interposed a small diaphragm with a $^3/_{16}$-inch hole for the passage of the sand and, in place of the tapering valve-plug, has substituted a flat cap. This alteration is shown in Fig. 2.

In operation, this valve stem was screwed up $^3/_8$ of an inch above the surface of the diaphragm and care was taken to see that it was raised the same amount each time, so as to secure uniform sand flow. This constitutes one of the weak points of the process, or rather the apparatus. There was no way of knowing whether the sand was feeding through the diaphragm at the same rate in each test, and as a matter of fact the amount of sand used did seem to vary more than could be accounted for by other irregularities of operation. Some kind of mechanical agitator of the sand in the tank, especially immediately about the point of escape would undoubtedly reduce this source of variation to a negligible factor.

The diaphragm wears slowly from the rapid flow of the sand through it and ought to be replaced at stated intervals. Near the end of our series, the old diaphragm was replaced by a new one, but no difference could be detected, so the old one was put back. In regular use, a new diaphragm every 100 tests would prevent this source of variation from becoming of importance.

The sand in the tank is kept under pressure and, probably, under slight motion, by the compressed air, which is admitted at the top and which escapes out at the bottom with the sand. Without this provision, the sand would not feed against the back pressure of the air in the injector. The injector is a compound one, the first jet acting as a mixer, and the lower one as a forcing jet.

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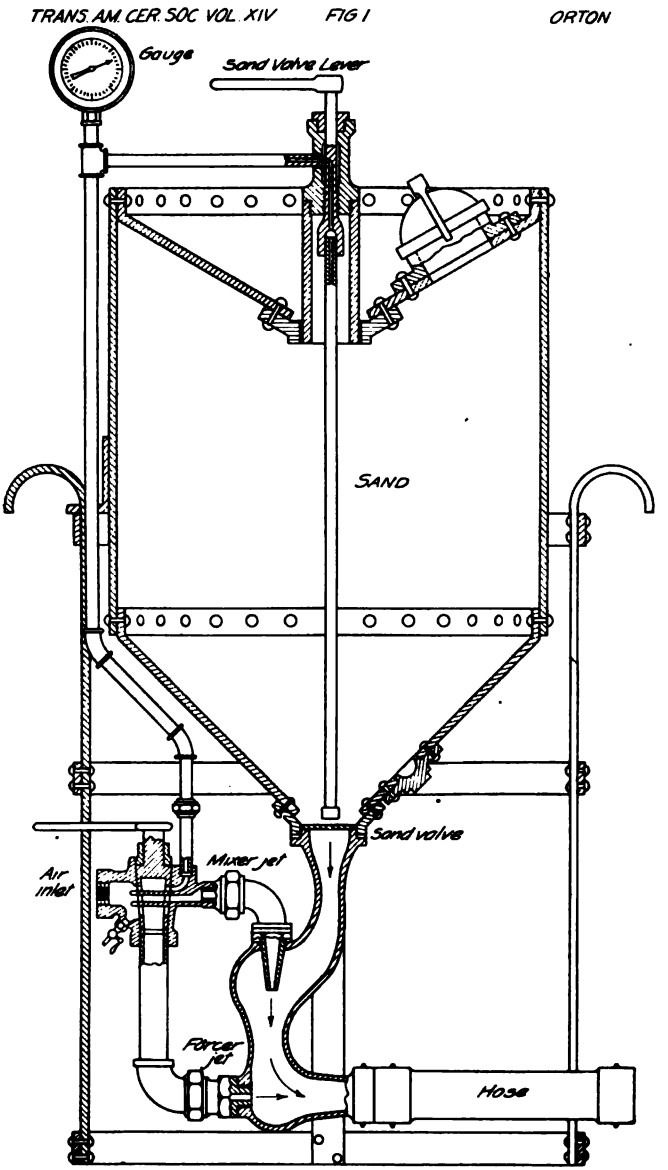

CROSS SECTION OF
THE DRUCKLIEB INJECTOR SAND BLAST APPARATUS

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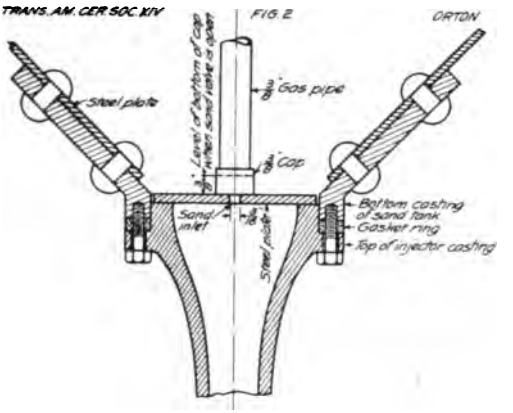

The Cabinet.—Besides the sandblast apparatus, there was required a dust-tight cabinet, in which the samples were exposed, and a rotating apparatus to secure uniformity of attack. This equipment is shown in Fig. 3.

The cabinet was made of wood in this instance, but a sheet metal one would be much better. If wood is used, it should be two thicknesses of matched flooring with paper between. At the bottom of the tapered bottom of the cabinet a valve for discharge of the sand is provided, and on the side of the cabinet a door for insertion and removal of the test pieces, etc. These openings should be gasketed with thick soft felt. The dust-laden air must be provided with a vent leading out of doors, or the work room will speedily become uninhabitable.

Holding and Rotating the Test Piece.—The arrangement for holding the test piece in position is a chuck, consisting of two plates of cast iron 9½ inches in diameter and held a fixed distance apart by 3 studs, spaced 120° apart. On these three studs a third cast iron plate slides loosely backward and forward. To clamp a brick in position against the outer, perforated plate, the loose plate is pushed up against it and a long threaded nut or sleeve, which works upon a stud set into the inner plate, is run out till it brings the plate hard up against the brick. The gasket between the face of the brick and the standard iron diaphragm

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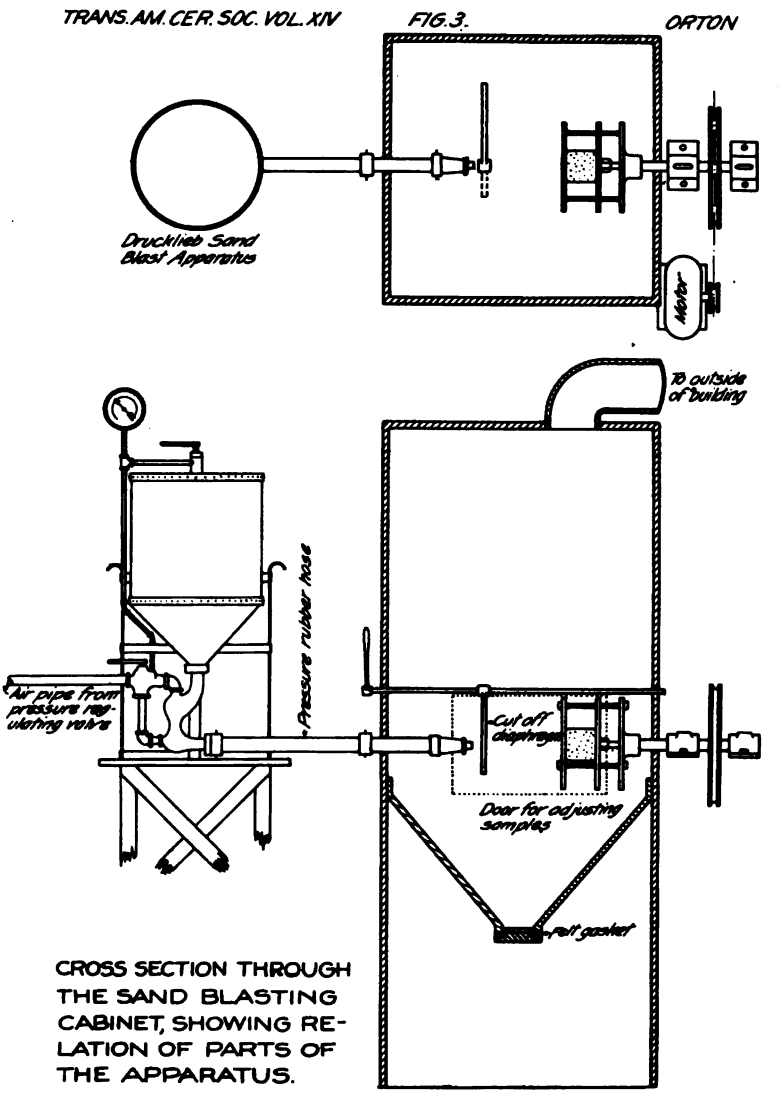

CROSS SECTION THROUGH THE SAND BLASTING CABINET, SHOWING RELATION OF PARTS OF THE APPARATUS.

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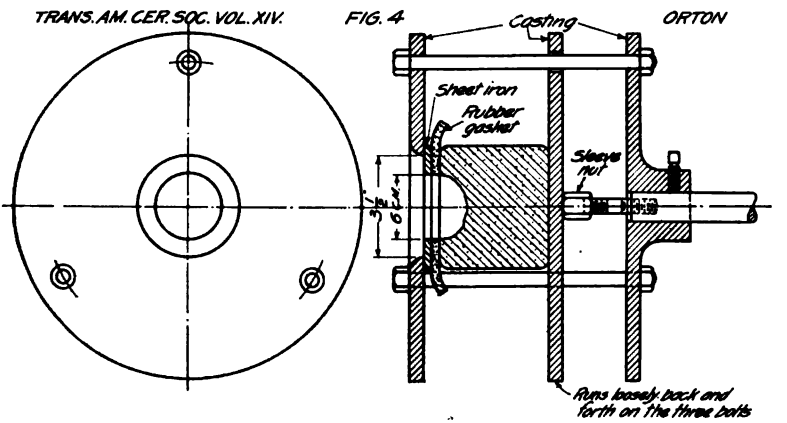
affords a soft spongy bearing, which prevents the brick from slipping, so that no great pressure is required (see Fig. 4).



The chuck was revolved at 80 r. p. m. while the test was in progress by means of a small motor, so that the cutting was very uniformly distributed.

The Template.—The template which regulates the area of attack is of $^1/_8$-inch sheet steel, and the hole in it is 6 centimeters in diameter. The template had to be placed on the center line of the chuck, or the brick would be thrown into and out of the main intensity of blast as it revolved. The template wore pretty rapidly, but its diameter usually *decreased* by the battering in of the metal, instead of increasing by the cutting out of the metal. It also warped out of shape, and had to be discarded from that cause. Whenever the hole had changed in diameter by 1 millimeter, or the template was so warped that it would not be brought flat on the surface to be worn, the template was discarded. It usually lasted about 10 runs, or 30 minutes of actual sandblasting.

The Sand Nozzle.—The sand was conveyed from the injector through a $1^1/_4$ inch rubber pressure hose. This hose clamped on to the injector with a good strong brass coupling. On the other end, the nozzle was coupled. The nozzle itself was cast iron, case hardened, with an aperture ½ inch in diameter. This aperture cut out pretty fast; the iron varied in hardness and the

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sand in cutting power, but whenever the nozzle had enlarged by $^1/_{32}$ of an inch, it was discarded. Nozzles averaged about 10 runs apiece. Nozzles of smaller and larger diameter than ½ inch were tried; the smaller cut a pit of irregular cross-section, the margins being separated from the center by a well defined line. Evidently, the cone of flying sand was not of equal vigor over the whole area, and the area of maximum cut was not equal to the 6 cm. hole in the diaphragm. With a nozzle larger than ½ inch, the sand cut uniformly, but the supply of air was not adequate to supply the machine at uniform pressure over the 3 minutes' run.

The Shield.—In order to exactly mark the beginning and end of each cutting period, a shield, fastened rigidly to a rod, was hung in front of the nozzle. By rotating the rod from outside the cabinet, the shield was moved aside from the line of the discharge. The time given for an actual cutting was 3 minutes, and by getting the apparatus into full operation and then suddenly shifting the shield aside, the start and stop could be regulated to a nicety.

The Air Pressure.—The compressed air was furnished by a compressor of rather small capacity for sandblast work. It had a tank in the engine room which acted in the double capacity of a reservoir and a water separator. A smaller tank near the sandblast apparatus, which was located at some distance from the engine room, also served as second reservoir. The pressure employed was kept at 20 lbs. as uniformly as possible; a regulating valve on the main air supply pipe made this easy, except when too large a nozzle was used. The gauge read up to 30 lbs.

The Sand.—It was the original intention to use the Ottawa Silica Company's sand, obtained by screening through a 20-mesh screen, and again on a 60-mesh screen, and using that which had passed the 20 and had lodged on the 60. After use this was to be re-screened between 20 and 60-mesh and a mechanical analysis run and compared with the original. If the mean size was found to be finer, it was to be toned up with new sand of 20–30 mesh grade from the original source of supply. This project was carried out, but with unsatisfactory results. An analysis of the sand before and after use showed as follows:

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Mesh	Before use	After use
20–30	11.2	9.2
30–40	44.0	41.0
40–50	15.8	17.8
50–60	11.1	13.6
60–80	4.8	6.2
80–	11.5	10.0

Some of the same sand was then screened between 20–40 mesh, and tried in the machine. The cutting power was found to be much decreased, and the air pressure was lower, because the sand was relatively more porous, *i. e.*, it had bigger gains and more interstitial spaces. This clearly showed that the sand was a factor of great importance and that no sandblast tests could be comparable in which this factor was not most closely standardized.

The next tests were made upon the Ottawa sand screened between 20 and 30-mesh, which is the sand used in standard cement tests. It required 3 minutes' blasting with this size to cut as much brick as was cut in 2 minutes with the 20–60 size of the same sand. After each run, the sand was screened again to take out the fine grains resulting from the process. The used sand was renewed by mixing in fresh sand at frequent intervals.

Experiments were made to determine whether a fresh lot of 20–30 Ottawa sand would give different results from a similar lot of the same sand used several times and then carefully screened to 20–30. The experiments were not extensive enough to prove the point but, so far as they went, tended to show that the used sand gave a little more active wear than the fresh.

After these experiments to learn the effect of variations in sand had been completed, the brick tests were run, great pains being taken to keep the treatment as uniform as possible. While the treatment did vary a little, it is thought that the errors introduced from this cause were not considerable and could not possibly change the general findings.

The quantity of sand required per test was about 20 lbs. The drum of the machine held about 40 lbs., and of this about 30 lbs. would feed out at an apparently regular rate; but the last 10 lbs. could not be depended upon.

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The Duration of the Test.—After testing a variety of substances, such as mortars, soft bricks, hard bricks, slag bricks, natural stones, etc., to get some sort of a comparative basis upon which to work, the figure of 3 minutes was arbitrarily selected for the standard test. In as little as 20 seconds, the blast would cut through 3 or 4 inches of well-seasoned lime mortar. In one minute it would cut two inches deep in a soft-burnt common brick. On a good, hard, vitrified paver, the depth of the excavation in 3 minutes was from ½ inch to $^3/_4$ or even an inch. It was not easily feasible to make comparisons in terms of volume excavated, on account of the variable shape of the hole made in different kinds of bricks. It was necessary, therefore, to compare the excavations by the loss in weight of the brick treated. The bricks were all weighed carefully on a torsion balance, to one gram, before and after the blasting.

The Final Conditions Used.—Unless otherwise stated in the notes, the following conditions were maintained:

Sandblast test.
- Sand—Ottawa Silica Company's 20–30 mesh—sifted after every test.
- Sand valve—$^3/_{16}$ hole in diaphragm—stopper raised $^3/_8$ inch.
- Sand nozzle—½ inch in diameter—changed when it wore to $^{17}/_{32}$ inch.
- Air pressure—20 lbs. per square inch.
- Area attacked—circle 6 centimeters in diameter.
- Distance between nozzle and brick—12 inches.
- Duration of test—3 minutes.
- Losses compared by loss of weight in grams.

Rattler test.
- The conditions specified by Blair and Orton, in report to American Society for Testing Materials, Vol. XIV, p. 776, and adopted by National Paving Brick Manufacturers' Association.

THE RESULTS OF THE TESTS.

The Bricks.—The bricks upon which the sandblast tests were carried out comprised 58 different lots, all of which had been previously tested by the rattler process. Of these 58 samples, 41 were paving blocks, and the 17 remaining were building

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bricks. They naturally showed various degrees of wear. In the case of the better grade of paving blocks, where the rattler losses had not exceeded 20 or 22 per cent., the individual bricks had lost corners and edges pretty generally but retained plenty of surfaces upon which the 6 centimeter perforated template would fit snugly. In the case of some of the softest paving blocks and the majority of the building bricks, the surfaces were worn rounding, so that the template could not obtain a uniformly flat bearing. The sand did not leak around the edges of the template in these cases and cause increased wear. The edges of the holes were sharp after the test. The only inequality, therefore, between those bricks which presented a virtually flat surface for attack and those of rounded surface was the slightly different distances between the different parts of the latter and the nozzle of the sandblast. It is not believed that these distances varied enough to make any sensible difference, and any such that existed would probably be in favor of the rounded bricks, instead of against them.

From each of the 58 lots of brick represented by 2 charges of 10 each, or 20 individual bricks, three bricks were selected for the sandblast test. They represented one of the harder bricks, one of the softer ones, and one seeming to represent the average. It would, of course, have been preferable to apply the sandblast test to all of the bricks of each charge, to get a more perfect comparison and better averages, but this would have made the test too costly. As it was actually put through, about 200 sandblast tests were made. All paving blocks were tested upon the edge, or surface which would be exposed to wear in the street if used as pavers, except where so badly worn that no suitable area could be found on the edge. Building bricks were tested on the side instead of the edge.

The Action of the Sandblast.—The sandblast cuts, with astonishing rapidity, into any ceramic material. The rate of cutting, however, varies very widely. In general, the action is slowest on dense, fine-grained or amorphous, hard bodies like glass, and most rapid in porous, granular, soft bodies like mortar or soft burnt clay wares. As a mode of exposing the extent to which the constituent parts of a clay body are bound together

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TABLE I.—RESULTS OF THE SANDBLAST AND RATTLER TESTS.

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
2 m	Shale. Paving block	16.97	69	..	No. 1 is hardest burned.
		17.33	75	..	
		...	77	..	
	Averages.....	17.15	74	..	
6_2	Shale. Paving block	17.48	79	..	No. 1 appears softer than other two.
		17.23	69	..	
		...	69	..	
	Averages.....	17.35	72	..	
12_2	Shale. Paving block	17.60	64	..	The second brick seemed the softest. The third brick had suffered worst in the rattler test. The extra test was run with sand which had been used several times without sifting.
		17.48	74	67	
		...	70	..	
	Averages.....	17.55	69	..	
15_2	Shale. Paving block	18.53	82	..	The second brick appeared the densest. The first brick seemed of more open structure than the others, from lack of pressure, or use of too much water in tempering, or some such cause.
		20.34	65	..	
		...	75	..	
	Averages.....	19.43	74	..	
19	$^2/_3$ shale, $^1/_3$ plastic fire clay. Common brick	63.23	174	..	Third brick is the softest burned. These were hand-moulded building bricks. They were tested on the side.
		58.27	172	..	
		...	221	..	
	Averages.....	60.75	189	..	
22	Shale. Building brick	36.30	92	..	No. 1 appears the softest, No. 3 is the hardest burned. These were hard burned for building bricks, but not designed to stand rattler treatment.
		41.57	80	..	
		...	70	..	
	Averages.....	38.93	81	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
26	Alluvial clay. Undersized paving block	38.15	81	..	No. 3 is the softest burned and was the worst damaged in the rattler. These bricks are very badly laminated; the texture of the body is dense but sandy.
		39.97	85	..	
		...	94	..	
	Averages.....	39.06	87	..	
29	Shale. Paving blocks	17.13	67	82	The second series of tests was run upon the same bricks as the first. Failure to check could not be explained.
		20.51	67	85	
		...	61	65	
		...	...	68	
	Averages.....	18.82	65	..	
34_2	Shale. Paving blocks	25.27	109	..	Brick No. 3 was hardest burned but was much the worst damaged in the rattler test.
		27.39	100	..	
		...	86	..	
	Averages.....	26.33	98	..	
36_2	Shale. Paving blocks	33.22	95	..	These blocks were not mechanically well-made. They were hard burned, but brittle.
		33.89	81	..	
		...	92	..	
	Averages.....	33.55	89	..	
39_2	Fire clay. Paving blocks	23.40	111	..	No. 1 was yellow in color. No. 2 and 3 were blue or dark gray. Duplicates check nicely.
		22.19	79	80	
		...	78	83	
	Averages.....	22.79	89	..	
44	Fire clay and shale mixed. Paving blocks	16.53	72	..	
		17.72	68	..	
		...	66	..	
	Averages.....	17.13	69	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
45₂	Fire clay and shale, mixed. Paving blocks	16.31	68	..	
		17.34	73	..	
		...	76	..	
	Averages.....	16.82	72	..	
47	Building brick. Surface clay	54.99	136	..	No. 1 was soft burned. No. 2 and 3 were hard burned.
		63.45	98	..	
		...	95	..	
	Averages.....	59.22	110	..	
49	Building brick. Sandy shale and surface clay	51.71	235	..	Sand blast cut entirely hrough brick in 3 minutes. These bricks had not vitrified and were entirely unsuited for anything but common building purposes.
	Averages.....	...	...	..	
53	Shale. Paving blocks	28.40	119	..	No. 2 appears harder burned than the others.
		24.94	76	..	
		...	107	..	
	Averages.....	26.67	101	..	
58	Shale. Paving blocks	26.92	119	..	No. 1 looks over-burned.
		28.20	93	..	
		...	92	..	
	Averages	27.56	101	..	
62	Shale. Paving blocks	25.46	139	..	No. 1 is the softest burned.
		24.47	110	..	
		...	117	..	
	Averages.....	24.96	122	..	
67	Shale and fire clay mixture. Paving blocks	22.50	95	..	No. 2 is the softest burned.
		21.51	112	..	
		...	96	..	
	Averages.....	22.01	101	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
70	Shale. Paving blocks	24.23	98	..	No. 3 seems the hardest burned.
		21.99	90	..	
		...	87	..	
	Averages.....	23.11	92	..	
73	Shale. Common bricks	37.90	131	..	This size has excessive wear in the rattler test, even when made of good material. This sample was not of very good quality—too sandy.
		36.94	108	..	
		...	101	..	
	Averages.....	37.41	113	..	
75₂	Shale. Paving blocks	22.64	82	..	
		23.71	75	..	
		...	95	..	
	Averages.....	23.18	84	..	
80	Shale and fire clay, mixed. Common brick size. Stiff-mud process	26.07	83	..	No. 3 is redder in color than the others. No. 1 and 2 are somewhat buff. These bricks stand an excellent test, considering their size, in the rattler.
		24.52	93	..	
		...	113	..	
	Averages.....	25.30	96	..	
82	Shale. Common bricks size. Stiff-mud process	35.18	64	..	These bricks are very hard, but brittle—do not stand the rattler test satisfactorily.
		...	64	..	
		...	68	..	
	Averages.....	...	65	..	
84	Shale. Common brick size. Stiff-mud process	23.03	99	..	These bricks stand an excellent rattler test, for their size.
		25.44	89	..	
		...	93	..	
	Averages.....	24.23	94	..	
86	Shale. Paving blocks	25.10	80	..	No. 3 is the hardest burned. This block is burned hard, but is brittle and given a poor rattler test.
		28.36	71	..	
		...	66	..	
	Averages.....	26.73	72	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
89	Shale. Common brick size. Stiff-mud process	...	134	..	Not intended for paving brick.
		49.63	137	..	
		47.29	189	..	
	Averages.....	48.46	153	..	
91	Fire clay. Paving brick. Common brick size	24.80	87	..	No. 1 is harder burned than the others.
		...	104	..	
		...	107	..	
	Averages.....	25.42	99	..	
94	Fire clay. Paving blocks	20.64	99	..	These blocks are not as vitreous as many, but they have a dense close grain and are very uniform. Second test was made on opposite side of brick No. 2.
		18.93	101	105	
		...	105	..	
	Averages.....	19.78	102	..	
97	Fire clay. Paving blocks	21.72	71	67	Second test was made on brick No. 2, with sand which had been used some time. Pressure varied somewhat.
		...	72	and	
		20.79	74	79	
	Averages.....	21.25	72	..	
101	Fire clay. Common brick size. Stiff-mud process	29.50	95	..	Brick No. 1 seems purer fire clay than the others, which contain shale particles.
		31.81	117	..	
		...	131	..	
	Averages.....	30.65	114	..	
106	Shale. Common brick size. Stiff-mud process	36.40	112	..	
		35.20	120	..	
		...	125	..	
	Averages.....	35.80	119	..	
108	Shale. Paving blocks	37.14	135	..	
		35.04	164	..	
		...	140	..	
	Averages.....	36.09	146	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
111	Shale. Paving blocks	22.67	110	..	No. 1 appears softer than the others. No. 3 much the harder burned.
		23.37	87	..	
		...	75	..	
	Averages.....	23.02	91	..	
114	Fire clay. Paving blocks	19.71	81	..	No. 3 the softest burned.
		18.04	80	..	
		...	92	..	
	Averages.....	18.88	84	..	
117_2	Shale. Paving blocks	23.58	80	..	The second test was on the other side of the brick, near the middle. This brick has a dense but brittle structure.
		23.43	80	..	
		...	63	72	
	Averages.....	23.50	74	..	
120_2	Shale. Paving blocks	20.43	63	..	No. 3 appears much softer than the other two.
		19.23	61	..	
		...	84	..	
	Averages.....	19.82	69	..	
123	Fire clay. Paving blocks	19.15	75	..	No. 1 has a better appearance than the other two.
		15.66	92	..	
		...	92	..	
	Averages.....	17.40	86	..	
126_2	Shale. Paving blocks	15.92	77	..	
		16.20	73	..	
		...	79	..	
	Averages.....	16.06	76	..	
129_2	Shale. Paving blocks	21.76	75	62	The second brick had lost most heavily in the rattler test. The bricks are all dense but show bad machine structure.
		22.02	89	..	
		...	63	..	
	Averages.....	21.89	76	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
132	Shale. Paving blocks	26.38	70	81	Brick No. 3 is softer burned than the others. Structure is not good for any of them.
		25.90	73	..	
		...	104	103	
	Averages.....	26.14	82	..	
136	Shale. Paving blocks	22.16	109	..	
		22.15	112	..	
		...	99	..	
	Averages.....	22.15	107	..	
139	Fire clay. Paving blocks	23.91	98	..	
		21.73	95	..	
		...	99	..	
	Averages.....	22.82	97	.	
142	Fire clay. Paving blocks	35.39	115	..	Brick No. 1 appears softer than others. The structure of this set is not good. Over-burned.
		33.33	99	..	
		...	103	..	
	Averages.....	34.36	106	..	
145	Shale. Paving blocks	21.99	97	..	
		22.16	108	..	
		...	96	..	
	Averages.....	22.07	100	..	
148	Shale. Paving blocks	16.80	70	..	The second brick lost most in the rattler.
		16.99	82	..	
		...	60	..	
	Averages.....	16.89	73	..	
152	Shale. Paving blocks	26.11	113	..	
		26.75	106	..	
		...	111	..	
	Averages.....	26.93	110	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
155	Shale. Paving blocks	27.67	83	..	These bricks appear brittle.
		27.94	74	..	
		...	90	..	
	Averages.....	27.80	82	..	
158	Shale. Paving blocks	21.26	68	58	This brick, No. 1, has a better appearance than the others and has withstood the rattler test better. These bricks show mechanical defects.
		21.01	66	..	
		...	61	..	
	Averages.....	21.14	65	..	
163	Shale. Paving blocks	21.94	65	..	No. 3 is the softer burned.
		26.70	59	..	The bricks are dense, but appear brittle.
		...	77	..	
	Averages.....	24.32	67	..	
166	Shale. Paving blocks	19.93	79	..	The bricks were 5 inches deep, and were tested on the side instead of the edge.
		19.30	84	..	
		...	78	..	
	Averages.....	19.61	80	..	
169	Shale and surface clay. Common brick size. Stiff-mud process	30.99	133	..	
		30.18	131	..	
		...	143	..	
	Averages.....	30.54	136	..	
171	Shale. Common brick size. Stiff-mud process	41.00	66	..	No. 1 is the hardest and No. 3 the softest. Hard burned shale. Brittle.
		...	86	..	
		...	93	..	
	Averages.....	...	82	..	
174	Shale and surface clay. Common brick size. Stiff-mud process	26.73	103	106	Hard burned shale. Brittle.
		34.00	100	77	
		...	72	72	
	Averages.....	30.76	92	..	

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TABLE I.—(*continued*).

Designation of brick sample	Kind of clay and kind of brick	Results of rattler tests. Per cents lost	Results of sandblast tests. Grams lost	Extra sandblast tests. Grams lost	Explanatory notes
179	Alluvial clay. Common brick size. Stiff-mud process	42.75	151	..	No. 1 is the hardest and No. 3 the softest. These brick not intended for other than building purposes.
		44.04	154	..	
		...	200	..	
	Averages.....	43.39	168	..	
181	Shale. Common brick size. Stiff-mud process	36.35	66	..	Hard burned shale, but brittle and unable to withstand the rattler test.
		37.68	72	..	
		...	72	..	
	Averages.....	37.01	70	..	
182	Shale and glacial clay. Paving blocks	14.80	63	75	Flaws evident where subjected to second test accounts for higher loss.
		18.86	60	..	
		...	60	60	
	Averages.....	16.83	61	..	
183	Fire clay. Paving blocks	25.48	80	..	These brick were brittle. No. 3 was the hardest burned and densest of the set.
		...	80	..	
		...	68	59	
	Averages.....	...	76	..	

into a silicate matrix, it is unrivaled. To a considerable extent, also, it is of use in developing the flaws, structural defects, laminations, lack of homogeneity, etc., in a clay body, for it cuts faster into all defects than into the solid portions.

There is no question but that the relative rate of destruction before the sandblast gives strongly characteristic data. The above table sufficiently demonstrates this fact, since the losses vary from 59 or 60 grams up to 236 grams in a three-minute test. As an illustration of the characteristic rate of wear and differences in structure revealed by the action of the sandblast, Fig. 5 is shown.

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A B C

FIG. 5

View of three bricks after exposure to sand blast for 3 minutes each. All conditions comparable.

Brick A. Stiff-mud building brick. Coarse texture; clay has been poorly ground; not well vitrified. Excavation $1^3/_4$ inches deep.

Brick B. Shale paving block Fairly dense body, well vitrified. Cut 1 inch deep.

Brick C. Paving block made in England from blast furnace slag. Exceedingly close dense body. Very hard. Depression $^3/_8$ inch deep.

Relative Performance of the Rattler and Sandblast Tests.—The mass of data in Table I is too large to permit the ready extraction of generalizations from it. Accordingly, a much abridged table, No. II, has been prepared. The results are arranged in the order of the magnitude of their losses in the rattler, in order that the corresponding losses by the sandblast may be more readily grasped. For convenience, the results in the paving block series are divided into groups.

From the table a very fair general agreement can be found between the results of the two methods. There are a large number of instances where the two processes check nicely. Out of 41 comparisons, about 30 give good checks. The other 11 or 12 comparisons are glaringly out of concordance, and the way in which both methods were able to check themselves shows that their failure to check each other is not accidental. However, since these discordant determinations constitute only about 25 per cent. of the total number, the general mean of the groups of ten consecutive determinations each still shows a notable concordance:

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TABLE II.—COMPARISON OF RATTLER TEST VS. SANDBLAST TEST.

FULL-SIZED PAVING BLOCK SERIES.

Designation of sample	Average rattler loss. Per cent.	Average sandblast loss. Grams
126	16.06	76
45	16.82	72
182	16.83	61
148	16.89	73
44	17.13	69
2	17.15	74
6	17.35	72
12	17.55	69
29	18.82	65
114	18.88	84
Average.....	17.34	71.5
123	19.15	86
15	19.43	74
166	19.61	80
94	19.7	102
120	19.82	69
158	21.14	65
97	21.25	72
129	21.89	76
67	22.01	101
145	22.07	100
Average.....	20.61	82.5
136	22.16	107
139	22.82	97
39	22.79	89
111	23.02	91
70	23.11	92
75	23.18	84
117	23.50	74
163	24.32	67
62	24.96	122
183	25.48	76
Average.....	23.53	89.9

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TABLE II.—(*continued*).

Designation of sample	Average rattler loss. Per cent.	Average sandblast loss. Grams
132	26.14	82
34	23.33	98
53	26.67	101
86	26.73	72
152	26.93	110
58	27.56	101
155	27.80	82
36	33.55	89
142	34.36	106
108	36.09	146
26	39.06	87
Average.....	29.84	97.6
COMMON BRICK-SIZED PAVERS AND BUILDING BRICKS.		
84	24.23	94
80	25.30	96
91	25.42	99
169	30.54	136
101	30.65	114
174	30.75	92
82	35.18	65
106	35.80	119
181	37.01	70
73	37.41	113
22	38.93	81
171	41.00	82
179	43.39	168
89	48.46	153
49	51.71	235
47	59.22	110
19	60.75	189

TABLE III.

	Average rattler loss. Per cent.	Average sandblast loss. Grams
1st ten samples.....	17.34	71.5
2nd ten samples.....	20.61	82.5
3rd ten samples.....	23.53	89.9
4th eleven samples.....	29.84	97.6

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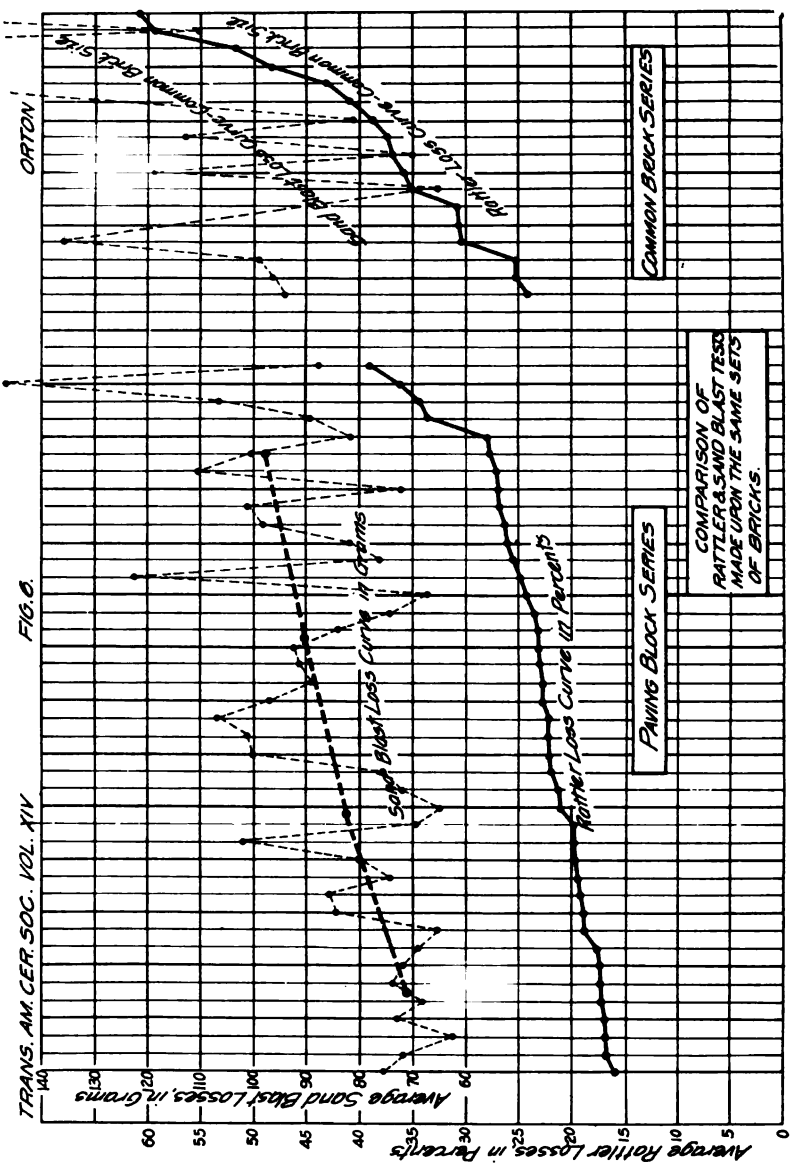

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These data seem to prove that the combination of properties which enables a paving brick to withstand the rattler test creditably will in general enable it to withstand the sandblast test creditably.

To still further strengthen the presentation of this point, Fig. 6 has been prepared, in which the data of Table II are expressed graphically. The heavy dotted line in the sandblast curve connects the average of the four groups given above. The substantial parallelism of the rattler loss curve and the curve of the mean losses by the sandblast is too striking to be ignored.

In the second part of Table II, when the data from the two methods are obtained from small pavers of common brick size, and from common stiff-mud building bricks not designed for pavers at all, this deduction is not so clear, though its general tendency is still the same. It certainly proves the above principle better than it proves another.

Looking next to the frequent cases of radical disagreement (constituting about 25 of the whole number tested), we find some samples which show a high sandblast loss with low rattler loss, and a large number of samples which show a low sandblast loss with high rattler loss. Table IV assembles the most striking of these instances:

TABLE IV.

Sample No.	Average rattler loss. Per cent.	Average sandblast loss. Grams	Variation from group averages of sandblast losses. Grams
94	19.78	102	+20
67	22.01	101	+19
145	22.07	100	+18
136	22.16	107	+17
26	39.06	87	—10
36	33.55	89	— 9
155	27.80	82	—15
86	26.73	72	—25
132	26.14	82	—15
183	25.48	76	—12
163	24.32	67	—22

Taking up now those cases where the sandblast losses are *plus* normal, we find that number 94 is a fire clay paver, of close

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uniform structure, not hard or well vitrified, but *tough* when it comes to resisting blows. Material from this immediate neighborhood, and of the same peculiarities, has been on the market for 25 years as paving brick and has an excellent reputation. The lack of hardness or vitreous quality allows it to cut away rapidly before the sandblast.

The second case, No. 67, is a brick manufactured from a mixture of fire clay and shale, and in burning the vitrification point of the shale is reached before that of the fire clay. The product contains grains of fire clay which are not bonded firmly into the mass, and which are soft or unvitrified still. In the rattler, this material is able to give a fairly good test owing to the toughness of the shale matrix. In the sandblast test, the fire clay grains cut away rapidly and so honeycomb the shale matrix that the latter follows soon after.

The third case, No. 145, is a shale brick, in which the shale itself is of good quality and vitrifies to a strong hard body. But in the clay bank is a stratum of sand rock which is very frequently mixed into the shale in quarrying. This material remains coarse after grinding—cannot be vitrified, and by its large volume-changes tends to work itself loose from the surrounding matrix. Thus the output of this plant at times is excellent, and at times not so good, depending on whether the sand rock is excluded or not. The sandblast test will promptly make use of such a condition and will cut into the brick very rapidly. The rattler test will also cause extra wear, but the shale matrix will hold together enough to show a fair loss only.

Of the fourth sample, No. 136, little is known as to the conditions of manufacture or the raw materials. It comes from a new factory which has not yet established itself firmly in the market, and, doubtless, the raw materials and conditions of manufacture have varied a good deal.

Examining now the other class of cases where the sandblast data is *minus normal* we find the following:

No. 26 was a brick made from a fat plastic alluvial clay and was very severely laminated in the auger machine. It broke down rapidly in the rattler tests from these flaws and lamina-

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tions. It stood well in the sandblast test, because the clay was vitrified into a hard tight-grained dense body.

No. 36 was a shale paver, but was structurally unsound, owing to extensive laminations, and, moreover, was brittle and unable to resist impact. It resisted the sandblast well, because of its glassy vitrified nature.

No. 155 was a shale paver of which little is known except that it was brittle. The same may be said of No. 86.

No. 183. This was a fire clay paver, burned especially for the test, and overburned through anxiety to make a good showing. The same blocks, softer burnt, would make a fair showing in the rattler test. They had become brittle; they were hard, however, and stood a good sandblast test.

163. These blocks are shale, and ordinarily make a fairly tough product. In this case they were dense, vitrified and brittle.

These cases seem to the writer to clearly show the fundamental differences in action of the rattler test and the sandblast test. The first set of bricks will stand the former and will not stand the latter, because the bricks are tough, but are either not very hard or else have numerous soft spots scattered through a hard matrix. The second set of bricks will stand the latter and not the former, because they are hard, vitreous and glassy in texture, but are brittle or defective in mechanical structure or both.

In short, the sandblast really measures hardness and not toughness, *i. e.*, glass would resist sandblasting exceptionally well, but it would not resist rattling at all well. And while it is true that in general the better grades of paving bricks do become increasingly hard as they vitrify and at the end are both tough and hard, it is equally well known that many clays which burn to a very hard body, of glassy texture, are very weak and brittle when subjected to blows. Hence, it is clear that in any large number of comparisons of the two processes, we should expect to find just what we do find, *viz.*, general concordance between the results of the two tests, but, nevertheless, frequent and wide departures from concordance.

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Relative Merits of the Two Processes as Measures of the Quality of Paving Bricks.—It may easily be claimed that the curve shown in Fig. 6 is unfair, in that it arbitrarily assumes the rattler test as the basis of comparison; arranges the rattler results in progressive numerical order; and gives them an appearance of close harmonious agreement that is far from the truth; and similarly prejudices the sandblast test by showing a markedly jagged curve. It is beyond question true, that by assuming the sandblast test as the standard of comparison, its results could have been made to appear smooth and constant, and the rattler test jagged and inconsequent.

But, it should be borne in mind, that in seeking to make a comparison between the values of these two methods, we cannot set aside the fact that the rattler test has, by a continuous usage of over 20 years, and a somewhat careful and fairly well standardized usage of at least 10 years, established itself as a criterion, while the sandblast has no such standing. Rattler tests have been made to the number of many thousands, by many hundreds of engineers to whom the results have come to offer an intelligible meaning. It is possible to some extent to interpret rattler data into wearing value in street use.

The rattler process started with the absorption test, the cross-breaking test, the crushing test, the specific gravity test, the hammer test, the frost test, the grinding table test, and perhaps some others; but it has outlived them all, and remains today practically the only test used. All the others have either disappeared wholly from use in estimating paving material, or are used in a sporadic case here and there.

In interpreting rattler data, there is still room for honest difference of opinion. It is agreed very generally among engineers and brick manufacturers that the rattler test is a severe test, and that any brick which can endure this test creditably will with absolute certainty give a good account of itself in street use, if properly laid. The best bricks in the world will make a wretched street if not properly laid, but such failures are not chargeable to the bricks themselves. On the other hand, it is by no means agreed just where to draw the line between permissible and non-permissible rattler losses, or to say just how good

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a material must be or how poor it dare be and still justify use in a street.

It has long been recognized that the rattler measures toughness, *i. e.*, ability to withstand blows and friction, better than any other device. No one can really say what makes one rock tough and another brittle. It is not wholly a function of hardness, certainly, because any very hard bricks are brittle, and yet, hardness enters into it. It is not a matter of crushing strength for many dry-press bricks show phenomenal crushing strength, but no dry-press brick rattles well. It is not wholly a matter of elasticity, for glass, one of the most brittle of solids, is very elastic indeed, and yet, a lack of elasticity would surely be against the development of toughness. Whatever toughness may be, or may not be, it is the one quality or combination of qualities needful above all others in good paving bricks.

On the other hand, the sandblast test does not bring out by any kind of shock or other means the presence or absence of toughness. Its blows are infinitesimally little, but also infinitely numerous. They wear away, not by a blow, but by scouring.

Any hard body, be it brittle or tough, is able to make a good showing in such a test. Hence the answer of the sandblast in any given case, unless supported by supplementary data, gives no assurance of toughness. Beyond a doubt, hardness in paving bricks is generally associated with toughness. In the present series, this is true in about 75 per cent. of the large number of samples tested. But, if the sandblast test gives a misleading decision in 25 per cent. of the cases in which it is used, how long can any one depend upon it?

THE SANDBLAST TEST FROM THE ECONOMIC STANDPOINT.

The test is like the rattler test in requiring the closest kind of adherence to an empirical standard of procedure. Every minute factor of both tests has its influence, and no one can get comparable data who does not conscientiously watch every one of these factors. The sandblast test has even more variables than the rattler. It would require more, rather than less, skill to use it. This is certainly against its use.

In point of time required, the sandblast test, *if applied to a*

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sufficient number of bricks to get reliable averages, would be much the longer. One blasting can be made in a few minutes, but to get a series of results involves cleaning out, readjusting, etc. It would increase the time required to give an answer as to a given material's fitness to be accepted—often a very urgent matter in street building. The readiness of the rattler is one of its strong points of advantage. In point of cost, the sandblast test would save nothing. The frequent renewal of nozzles, diaphragms, templates, gaskets, etc., the constant wearing out and restandardization of the sand supply, and the cost of making the compressed air, would surely counterbalance the larger use of power and the heavy wear and tear on staves and shot in the rattler process.

The country has facilities for the sandblast test in very few commercial establishments and in practically no testing laboratories. It would be a long time before the method could come into general use even if its advantages were obvious and weighty.

CONCLUSIONS.

1. The sandblast method has no advantage on either technical or economic grounds over the rattler process as a mode of testing paving bricks for their resistance and wear.

2. The sandblast test measures hardness rather than strength or toughness, and while most good paving bricks are hard, it is entirely unsafe to make the hardness test the criterion of their excellence.

3. The greatest value of the sandblast as a laboratory tool is its ability to expose the structure of strong bodies, natural or artificial. For this purpose it is unrivaled.

DISCUSSION.

Mr. Brown: I agree with Professor Orton that the sandblast test measures the hardness and not the toughness, and that the rattler test measures the toughness. Also, I think that the rattler test shows up the laminations better than the sandblast. The sandblast test is on only a portion of the brick, while the rattler test is on the whole brick. In comparing the two tests,

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you notice the sandblast tests were made on three bricks, and the rattler tests were made on twenty bricks. I think if the sandblast tests had been made on twenty bricks there would not have been so much variation. The average would have fallen about the same way.

Mr. Orton: The sandblast figures as plotted are averages between three independent results. If we had found that those independent observations varied widely between themselves that would justify your conclusion; but as a matter of fact there was pretty close agreement between the individual sandblast tests made on any set of bricks.

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A THERMAL STUDY OF BORIC ACID-SILICA MIXTURES.

By A. V. BLEININGER and PAUL TEETOR, Urbana, Ill.

The subject of possible chemical combinations of silica and boric acid has received some attention in our Transactions,[1,2] and the question raised is interesting inasmuch as such mixtures possess most decidedly the character of glasses or solid solutions. Thermal analysis thus does not promise a fruitful field of investigation. However, of the two methods comprising thermal analysis, the determinations of the softening temperatures is of some interest in itself, since it gives us the general character of the fusion curve of the two components involved.

A thermal lag is not to be expected either in the heating or cooling curves. In the present work, a search was made, however, for such a point based on the statement of Binns, Trans. A. C. S., X, p. 158, in which he records a temperature increase upon the fusion of a mixture of boric acid and silica, due to some exothermal change. The present research deals, (*a*) with the determination of the softening points of SiO_2-B_2O_3 mixtures between the limits B_2O_3-$B_2O_3.3SiO_2$, (*b*) with the determination of heating and cooling curves and (*c*) with an investigation of the solubility of the fused glasses in water. The reagents used were chemically pure hydrous boric acid and silica, the latter being a B. & A. preparation which unfortunately contained several per cent. of sodium chloride and water. In the latter part of the series, fusions were made also with flint which had been passed through a 200 mesh sieve. The calculation of the mixtures was based upon the analyzed silica content, practically 97 per cent. The boric acid was fused, cooled rapidly and kept in a desiccator. It was crushed in a porcelain and pulverized in an agate mortar. Similarly, the silica was ignited and kept in a desiccator. The mixtures were ground together in the agate mortar and fused over the blast lamp in a 10 cc. platinum crucible kept covered during the heating. After some time, the yellow color of the mass disappeared, which seemed to be a measure of the completeness of the fusion. The cooled mass had an opaque

[1] Binns, Trans. A. C. S., Vol. X, p. 158.
[2] Singer, Trans. A. C S., Vol. XI, p. 676.

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but glassy appearance. The fused mixture was easily removed from the crucible by inserting a platinum rod and quickly cooling in cold water. Then the fusion was pulverized and screened through 80 and 150 mesh screens. The portion passing the 80 but remaining on the 150 mesh screen was used for the solubility samples. This was done in order that no great variations in the surface factor might affect the solubility of the several mixtures.

SOFTENING POINT DETERMINATION.

For this purpose, the fused mixtures of SiO_2 and B_2O_3, ground to a fine powder, were made up with a little water into small cones, and placed in an electric resistance furnace. The specimens were kept in position by means of platinum foil. Since in glasses practically no other criterion is available than the deformation point, the temperature at which the cones bent was taken to represent the softening point. Care was taken to raise the heat at a regular rate by rheostat regulation, and the temperature readings were made by means of a Pt-PtRd thermo-couple, the electromotive force of which was determined by the method of balancing against a standard cell by means of a potentiometer indicator.

Owing to the fact that by mistake water was used in making up the mixtures, some anhydrous boric acid reverted to the hydrous form. This, of course, made it troublesome to determine the deformation point of B_2O_3 owing to the evolution of steam and the resulting bubbling. With the addition of 0.1 SiO_2, the cones seemed to stand up apparently in good shape. The heat given off on adding water to the $B_2O_3.1.5SiO_2$ mixture was so great that the crucible could not be held in the hand. At the same time very little heat was evolved by the $B_2O_3.1.4SiO_2$ and the $B_2O_3.1.6SiO_2$ glasses. On fusing the $B_2O_3.1.5SiO_2$ mixture, it assumed a pink color.

It was soon observed that these glasses were quite viscous. This was illustrated by the fact that a twisted platinum wire on being lowered into the fused mass and again raised was found to draw out a ribbon of glass. It is not surprising, therefore, that the softening points could not be checked, in spite of the fact that the same rate of heating was followed as closely as possible.

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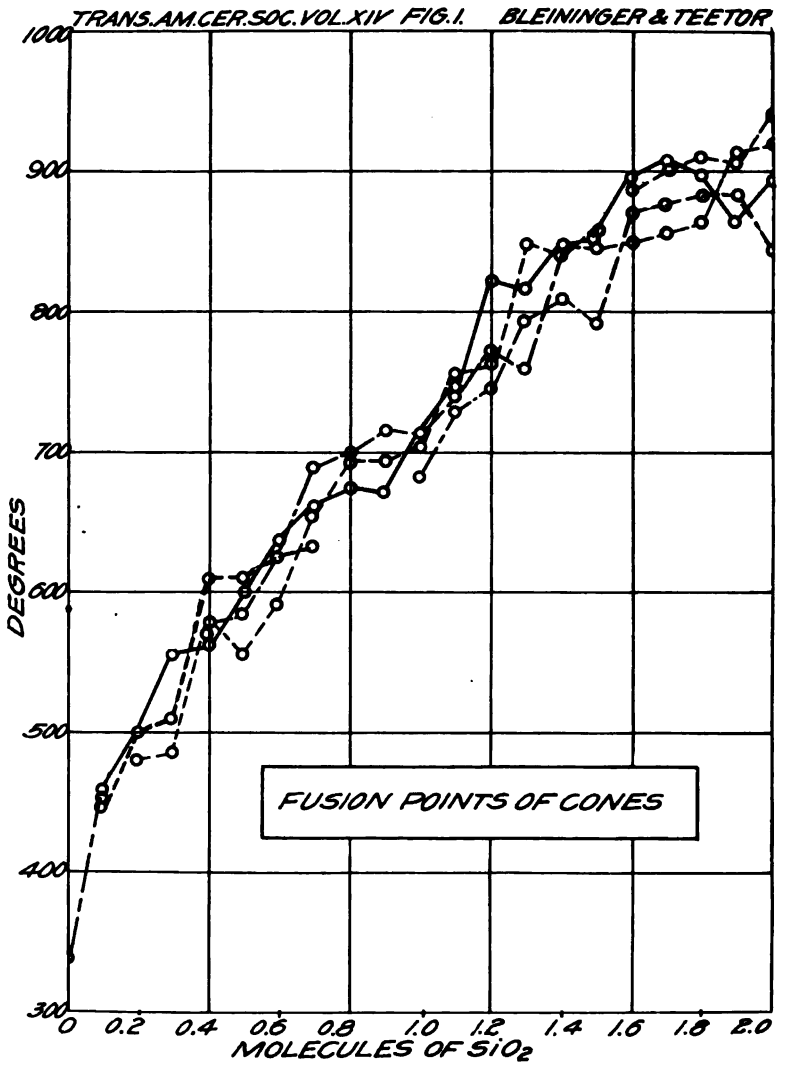

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In going over this part of the work four times, the results shown in Fig. 1 were obtained. The softening points of the mixtures beyond $B_2O_3.2SiO_2$ are not plotted since the divergence in this part of the series is still greater.

Softening point determinations were also made upon rods drawn from all of the fusions but these likewise gave extremely variable results, considerably lower than those obtained for the cones.

The evidence thus far collected makes it apparent that any reaction taking place under these conditions would be greatly hindered by the internal molecular friction.

HEATING AND COOLING CURVES.

A considerable number of heating and cooling curves were determined with special reference to the $B_2O_3.2SiO_2$ mixture. The latter was prepared from fused B_2O_3 and prepared SiO_2, and from fused boric acid and flint, passed through the 200 mesh sieve. In no instance was there a temperature acceleration or lag observed, and, hence, the observation of Binns was not checked. In Fig. 2, the heating curve in which the couple readings were made by means of a potentiometer indicator is shown. The junction was kept at 0° C. by means of ice. In Figs. 3 and 4, both the heating and cooling curves for prepared silica and flint mixtures as indicated by a Siemens and Halske recorder, making a contact every 16 seconds, are presented. It was observed that on fusing any mixture of B_2O_3 and SiO_2, *without* previous fritting, some vapor was expelled suddenly, carrying evidently a certain amount of boron. This happened also when both the boric acid and silica had been ignited separately to constant weight before mixing. Since Professor Binns used an optical pyrometer, it is quite possible that by focusing upon this vapor the readings were changed as observed by him.

SOLUBILITY DETERMINATIONS.

The different mixtures were fused and pulverized on cooling. The resulting powder was screened through the 80 and 150 mesh sieve. All material coarser than the 80 and finer than the 150 mesh was rejected. One gram samples were then weighed and put in stoppered 250 cc. Erlenmeyer flasks. These were placed

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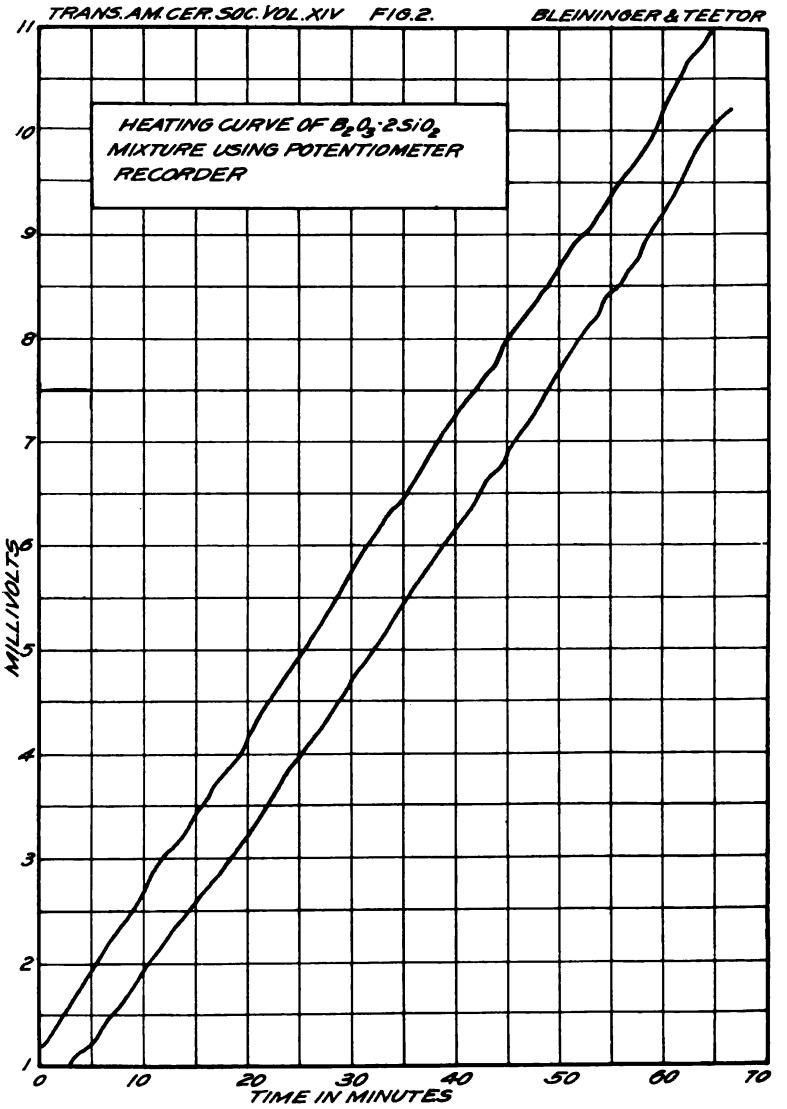

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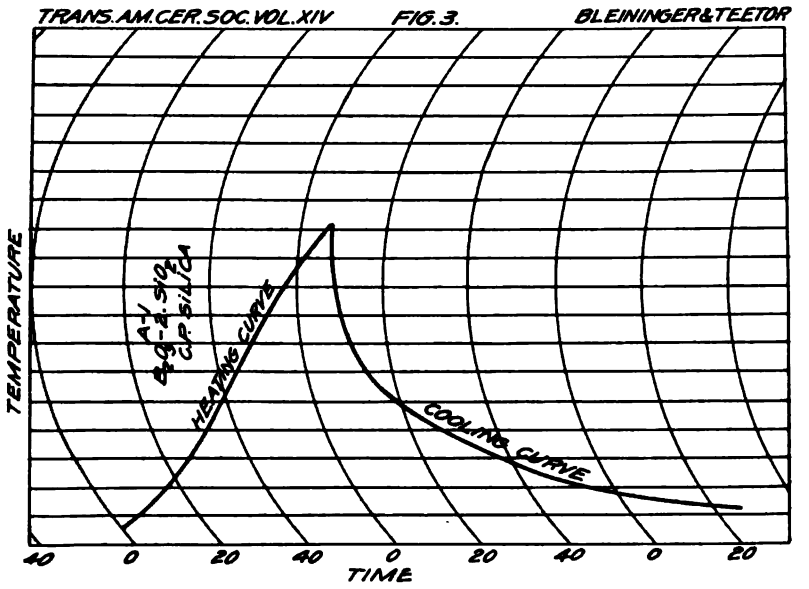

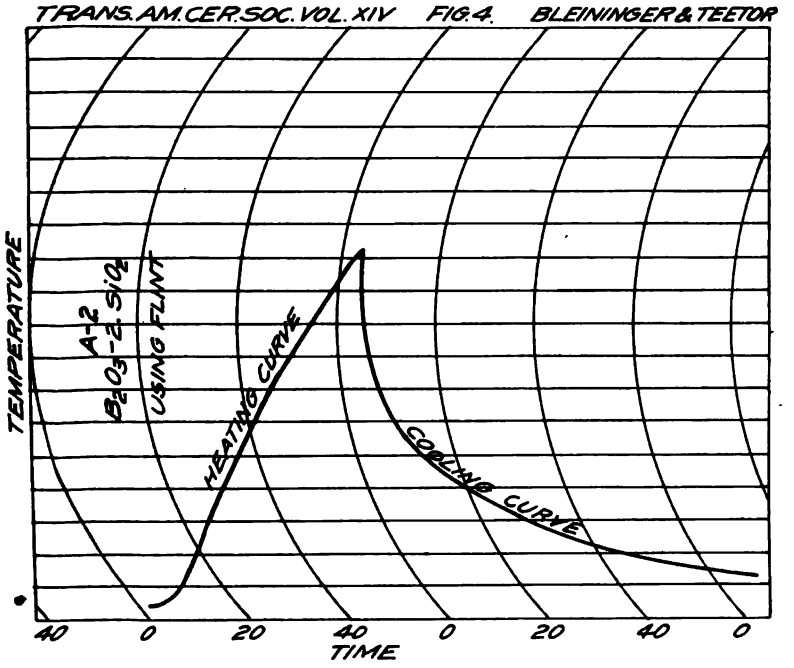

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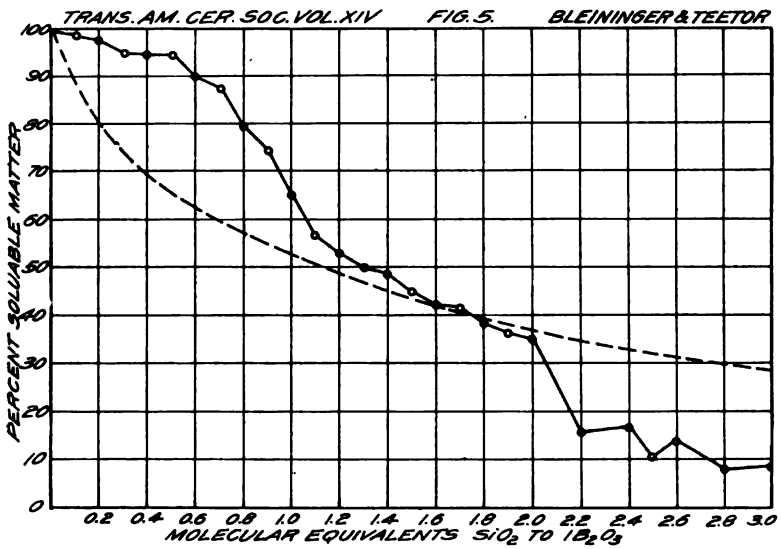
in a shaking machine together with 200 cc. of distilled water. After shaking for 10 hours and standing over night, the liquid was filtered off and the residue washed. Then 200 cc. of water was again added (including the wash water used) and the flasks were again shaken for one hour. The residue was again filtered and washed. After drying, the residues and paper were ignited and the weights determined. The insoluble matter in each case was brushed off and the paper burnt separately.

The weights of the residues are shown in the curve of Fig. 5.



It is seen that all of the boric acid was dissolved in the first of the series as well as some of the silica. At a point close to $B_2O_3.1.8SiO_2$, however, the solubility curve crosses the line indicating the percentage content of B_2O_3 (shown by the dotted line) which proves that some B_2O_3 has been rendered insoluble. This tendency increases with the silica content. At the molecular ratio 1 : 2 a decided drop occurs indicating the rapid formation of an insoluble glass. As to the cause of this sudden change, we can only conjecture at the present time. To establish the fact that a chemical combination has taken place would require the

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running of a parallel series using another criterion such as the specific gravity of the powder. At the present time, however, this evidence might be used to support the claim that we are dealing here with a solid solution representing a chemical union between the silica and the boric acid.

CONCLUSIONS.

Fused boric acid-silica mixtures are typical glasses possessing no definite deformation temperatures.

No thermal phenomena were observed, *i. e.*, there was no absorption or liberation of heat throughout the series B_2O_3 to $B_2O_3.3SiO_2$.

Boric acid when fused with silica first dissolves some of the latter. The amount of matter soluble in water decreases somewhat more rapidly than the B_2O_3 content. Between 2 and 2.2 SiO_2 a decided drop in the solubility of the glasses occurs, indicating that some B_2O_3 has been rendered insoluble. It is quite probable, although not proven, that a chemical combination might take place at this point. The gradual decrease in solubility might thus be ascribed to the formation of some of this combination at an earlier stage. At the point mentioned, a more rapid enrichment would thus take place.

DISCUSSION.

Professor Binns: I am interested in the results secured by Professor Bleininger. When I made the first experiments of this kind I expressly disclaimed any pretension to the ability called for by such work, and I based my chief claim as to the action of boron upon the practical issues as expressed in glaze composition. From this position, which has been confirmed by Dr. Singer and Mr. Stull, I have not had cause to retreat.

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THE BEHAVIOR OF GRANULAR LIMESTONE IN BURNED CLAY.

By CHARLES F. BINNS and MERLE A. COATS.

Prof. A. V. Bleininger two years ago read a paper before the Wisconsin Clay Manufacturers' Association on "The Function of Lime in Clays," which was published in full in the *Clayworker* of August, 1910. While Prof. Bleininger covered the ground more fully than it is now proposed to do, this paper is presented in order to bring the subject definitely before this society and to elicit discussion. The work has been done quite independently of Bleininger's investigation and any overlapping is but the natural consequence of similar work.

It is a fact well known to clay-workers that limestone in small pieces is the cause of serious trouble. The calcium carbonate is dissociated in the heat of the kiln, the carbon dioxide being driven off and the oxide left in the form of quick-lime. Upon exposure to weather this lime exerts its natural affinity for moisture and carbon dioxide; and obtaining these from the atmosphere, it swells and ruptures the clay body. Clay containing an appreciable amount of lime can rarely be burned to vitrification because of the sudden fusion which is apt to ensue. It follows, therefore, that the lime grains are, after burning, embedded in a mass which is more or less porous and which affords easy ingress to the atmospheric gases. The object of the present investigation was to determine: first, the smallest size of grain at which the limestone was dangerous; second, the amount of lime which could be present without causing harm; third, the effect of fire in destroying the power of the lime; and fourth, the possibility of treating the ware after burning so as to render the lime harmless.

An ordinary red-burning brick clay was chosen as the body. This happened to be a surface clay of slaking character from the carboniferous horizon. Used alone it burned to a clear red and to a common brick density at about cone 01.

A gray limestone used as a building stone was crushed and graded in the following sizes: 8–12 mesh, 12–20, 20–36, 36–55.

Of the largest grain limestone, 8–12 mesh, amounts of 1,

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3, 5 and 8 per cent., respectively, were added to the clay. Of each mixture 9 small bricks were made by the plastic process, using a wooden mold. Three of the bricks were burned at each of the cones 06, 03 and 01 in 18 hours. The same procedure was followed in the case of the 12–20 mesh. In order to test the effect of the German practice of soaking brick containing lime, one brick of each series was immersed in water for 30 seconds and another brick was soaked to saturation immediately on being drawn from the kiln. The remaining brick of the trio was left dry.

Each group of 36 brick was then arranged in order on a shelf in the laboratory, but there was no further treatment.

Fig. I.

After 20 days the first photograph, Fig. I, was taken. There is no serious damage except spalls on the surface until the 5 per cent. lime is reached. Of these the dry and dipped brick at the lower fires show signs of a weakened structure. Of the 8 per cent. series all the dry and dipped brick are crumbling, some of them being completely destroyed. The damage is rather less in the higher burn. None of the soaked brick, even with the highest content of lime, show any damage except the white spots on the surface where the lime grains are exposed.

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After 10 days more a second photograph, Fig. II, was taken. The spalling is worse in the members with the smaller content

Fig. II.

of lime and the disintegration of those with 5 or 8 per cent. has proceeded further. The soaked brick are still sound.

Fig. III.

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Another 10 days show no change except that the disintegration which had been before noted had gone further (see Fig. III). The soaked brick are still intact.

The next series consists of the brick containing 12–20 mesh lime in the same percentages as before.

In this case the first photograph, Fig. IV, was taken after ten days. Practically the same phenomena are observed but in a less marked degree. It should be noted that the dipping for 30 seconds has no effect at all. Sometimes the dry brick give way first and sometimes those that were dipped.

Fig. IV.

After 20 days the disintegration has progressed as in the former case, the higher fired brick standing up better than the lower (see Fig. V.)

Ten days more and the next photograph, Fig. VI, was taken. The story is the same with the increase in crumbling which would be expected. Here again the soaked brick stand unharmed, while those which were set up dry have gone to pieces and those which were only dipped are nearly as bad.

The fact that the smaller percentages of lime caused no damage even with the largest grain showed that there was no need to repeat these quantities with a smaller sized limestone.

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It also appeared that an immersion in water for so short a period as 30 seconds was practically without effect. In the next series,

Fig. V.

therefore, made up with 20–36 grain limestone, percentages of 5, 8, 12 and 15 were used and six brick only were set up, one at

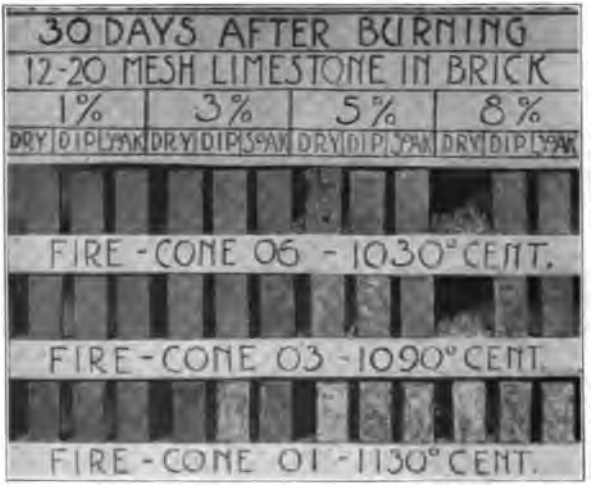

Fig. VI.

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each fire being dry, the other soaked. At the same time a series was made with 36–55 grain limestone, both groups of brick being treated alike.

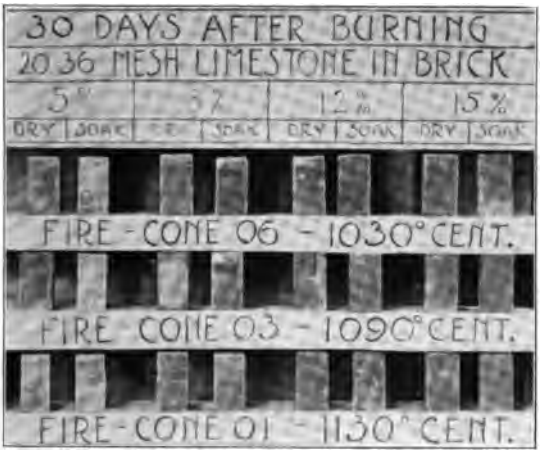

Fig. VII.

After standing for 30 days no marked change could be observed (see Fig. VII). A slight disintegration shows on the edges

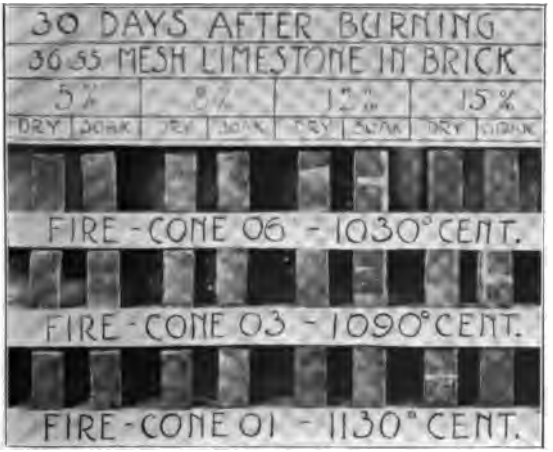

Fig. VIII.

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of the 15 per cent. dry brick at cone 01, this being the first occasion in which the higher fire is less effective than the lower. A possible explanation of this is that the larger percentage of lime has produced an open and more elastic structure at the lower fire and this has served to take up the expansion of the grains. In the higher fire the body has become more resistant and, hence, it gives way under pressure. It is probable that all the 15 per cent. dry brick will eventually fail though the soaked members still appear sound.

In the group containing 36–55 lime there has not yet appeared any disintegrating effect (see Fig. VIII).

CONCLUSIONS.

It appears from this study:

First, that lime grains as large as would be rejected by a 12 mesh sieve are objectionable even in small quantities, for though the brick may not be ruptured there is apt to be an unsightly spalling of the surface.

Second, lime grains which pass 20 mesh are admissible up to 3 per cent. of the weight of clay, but here also there is a likelihood of surface damage.

Third, that to be entirely safe the lime grains must be ground to pass a 36 mesh sieve, and that lime as fine as this may be present in a proportion as high as 12 per cent.

Fourth, that the danger of rupture from lime grains may be almost completely avoided by a saturation of the brick on being drawn from the kiln. This saturation appears to be more effective if the brick are in a very porous condition. Some of the members which were burned to a greater density exhibit some surface spalling, but brick were made and soaked ten months ago and are whole yet.

The fact that saturation with water prevents the crumbling of the brick is of such an interesting nature that some study has been devoted to it. Prof. Bleininger states that the lime on being treated with an abundance of water does not swell as much as the lime which draws the moisture from the air. This is not the experience of the writer. It has been found that a given quantity of granulated lime when wetted will expand suddenly

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and then shrink slightly though not to its former bulk. The same quantity of lime when exposed to the air will swell slowly though it does not reach the amount of expansion of the wetted lime.

Fig. IX.

In the experiment illustrated in Fig. IX, the same weight of freshly burned granulated lime was placed in each of two glass tubes and a dark line was marked level with the top of the lime. The tubes were set on blocks of plaster for support. Into the tube marked "wet" sufficient distilled water was poured to thoroughly slake the lime. The tube marked "dry" was not wetted but placed in a moist atmosphere. The expansion of the wet lime was sudden and was followed by a slight shrinkage of the mass. The dry lime slowly expanded but did not reach the volume of the other. It seems as though the sudden and complete saturation of the lime caused it to deliver a quick blow, like that of a hammer, upon the surrounding clay and that after this blow it had no further power. The dry lime, on the other hand, exerts a slow and increasing pressure which under the proper conditions is irresistible. Whether this explanation be the true one or not, it seems to present fewer difficulties than any other which has appeared.

DISCUSSION.

Professor Bleininger: The authorities on lime seem to agree that the lump expansion of lime in the presence of a larger amount is smaller than in the case of a smaller volume of water. This is all I know about it, and I am very much pleased that Professor

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Binns has done this work. I have been attending for several years the meetings of the National Lime Manufacturers' Association, and I find that they are up against the same propositions that we are with clays. Some of their evidence is, on the surface, contradictory.

Professor Orton: I have been very much interested in Professor Binns' paper, and I think it is valuable and suggestive. I recall one little instance, occurring some years ago, of a clay that was sent to me by one of the large clay machinery manufacturers. They had manufactured it into brick and had burned it. The resultant brick exhibited no signs of disintegration at first; but in a few weeks they had undergone an expansion which worked their complete destruction, until a brick would be nothing but a heap of granular particles. A study of this material showed that the rock which was causing the expansion there was not by any means a pure limestone. In fact it did not resemble a limestone in appearance, either in the burnt state or in the raw form. It contained only about 5 per cent. of lime, as I recall it, and this low percentage of lime was probably the reason for the slow crumbling, or the delay in the beginning of the crumbling process. I mention this instance merely to call attention to the fact that stones which are not limestone in the usual sense of the word, and which do not look dangerous to a clay, may still occasion just such troubles as real limestone does.

NOTE PREPARED AFTER READING THE PAPER.

Dr. Ries: Professor Binn's paper on the Effect of Lime Particles on Clay has interested me as one of my students was making a similar line of experiments last winter. There seems to be a slight difference in the results obtained, in that the lime seems to have acted less energetically in the case of the bricks tested by Professor Binns than it did on the bricks tested in my laboratory. As far as I can see at the present moment, I believe the difference may be explained by the fact that the same clay was not used by him and by me. The clay which I used was a rather dense burning one, while the clay which Professor Binns used was a more open burning material. This I think would account somewhat for the difference in results obtained.

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THE PRODUCTION OF BLACK SPOTS UPON TERRA COTTA GLAZES.

By CULLEN W. PARMELEE and RALPH HEIDINGSFELD.

The experiment which is to be described is an attempt at determining the most suitable composition of calcines of the oxides of cobalt, chromium and iron which will yield satisfactory black spots when applied on terra cotta glazes and slips.

Such black spots are used by those engaged in the manufacture of architectural terra cotta in order to imitate the appearance of polished granite.

The preparation of the colors was done by weighing separately each coloring oxide for each mixture. Each mixture was put into a crucible, and the whole series was calcined at cone 07 in a laboratory kiln, fired with soft coal. Subsequently the calcines were ground in a mortar, mixed with sufficient water so as to be readily taken up by a brush, and then spattered upon the surfaces of the various slips and glazes to be mentioned later. These trial pieces had been prepared from a terra cotta body of fire clays and grog, coated by spraying with underslips, some sprayed with a glaze and some left unglazed. The trials were burned in one fire in a laboratory kiln fired with soft coal.

The results of these trials are best understood by a study of the accompanying charts. We have attempted to indicate upon them the approximate boundaries of the blue, green, brown and black areas. Of course, it will be understood that some difficulty was experienced in locating these boundaries, since the areas are not sharply defined. For example, we found blue-blacks, green-blacks and brown-blacks, and blue-greens and green-blues, etc.; but within the areas of the blacks shown, will be found those calcines which yield blacks.

A study of the charts develops some interesting relationships. With glaze composition constant and underslip varying from 0 per cent. to 1 per cent., 2 per cent., 3 per cent., 4 per cent., 5 per cent., of whiting, we find that the area of the black spot increases with the increase of whiting up to 3 per cent. Further additions of whiting do not seem to be accompanied by increases in area. Compare charts Nos. 1, 2, 3, 4, 5 and 6.

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Charts Nos. 7 and 8 appear to confirm the foregoing conclusion since an increase of whiting from 3 per cent. to 4 per cent. in the slip shows about the same area.

Comparing charts Nos. 1, 9 and 10, we see the influence of varying the glaze composition. Glaze 148 seems to be least favorably inclined towards the development of black spots since the range of composition of the blacks is very limited, while glaze 184 is most kindly disposed.

Charts Nos. 11, 12, 13, 14, 15 and 16 show the effect of increasing content of lime introduced in the slip in the form of whiting. No glazes were used on these slips. The results appear to confirm the results shown on Charts Nos. 1 to 6 inclusive, namely, that an increase in lime up to a certain amount in the slip is followed by an increase in the area of blacks. Here we obtain, apparently, the maximum area of blacks with 4 per cent. whiting.

We shall not attempt any generalization from these results since the experiments cover rather a narrow field.

The compositions of the glazes and slips used were:

SLIPS.

	D_7	D_9	B_4	B_5	D_2
Ball clay Crossleys	25	25	15	15	25
China clay Eng. No. 7	20	20	20	20	10
Flint	30	10	20	10	40
Feldspar	25	45	45	55	25
Whiting. The lime content of each slip is indicated upon each chart					

GLAZES.

No.	MgO	BaO	CaO	K_2O	ZnO	Al_2O_3	SiO_2
148	0.1	0.1	0.5	0.3	...	0.56	3.08
184	0.1	0.1	0.4	0.4	...	0.56	3.08
108	...	...	0.2	0.4	0.4	0.56	3.08
7	0.3	...	0.1	0.2	0.4	0.35	4.10
3	0.2	...	0.3	0.2	0.3	0.25	3.32

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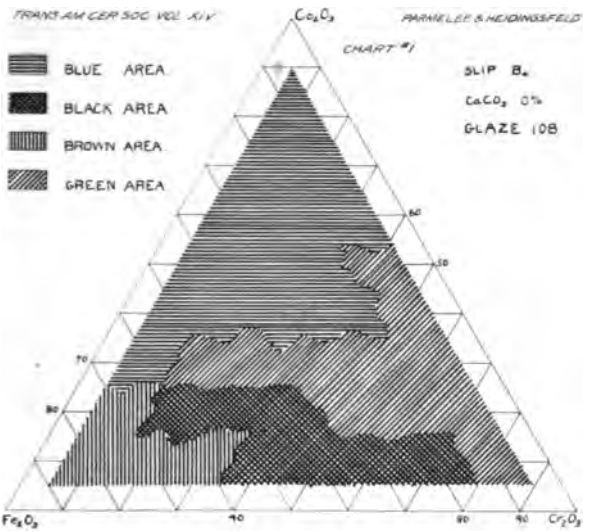

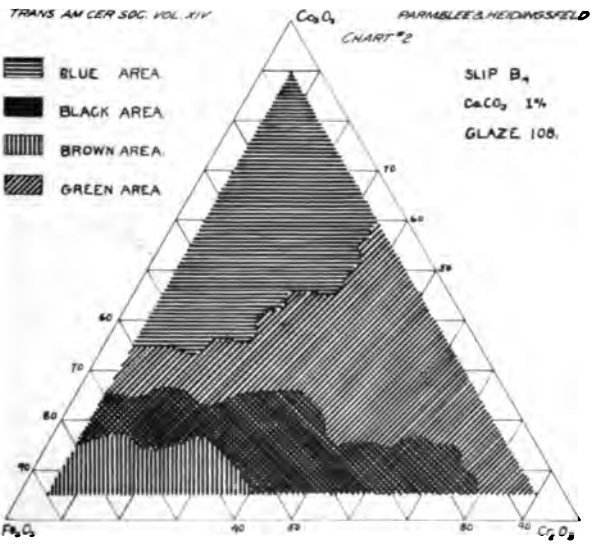

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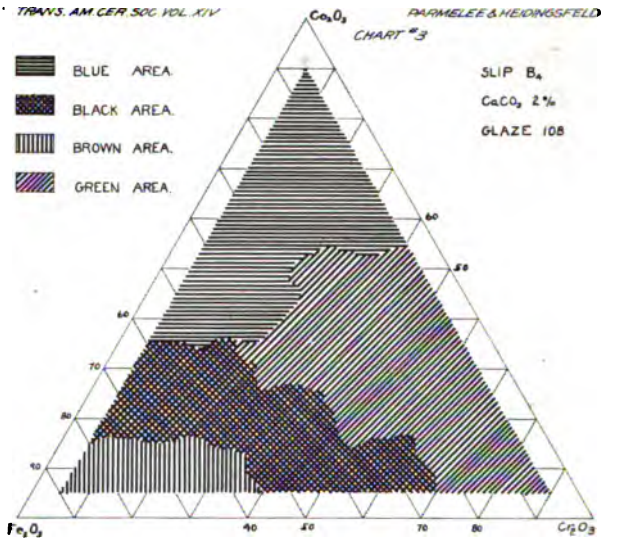

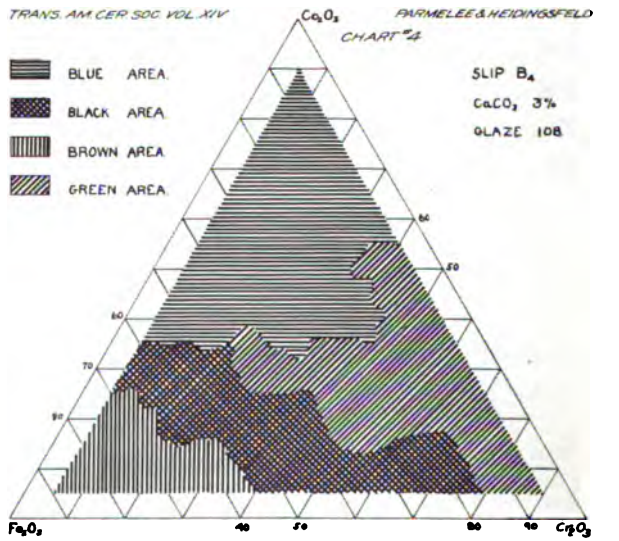

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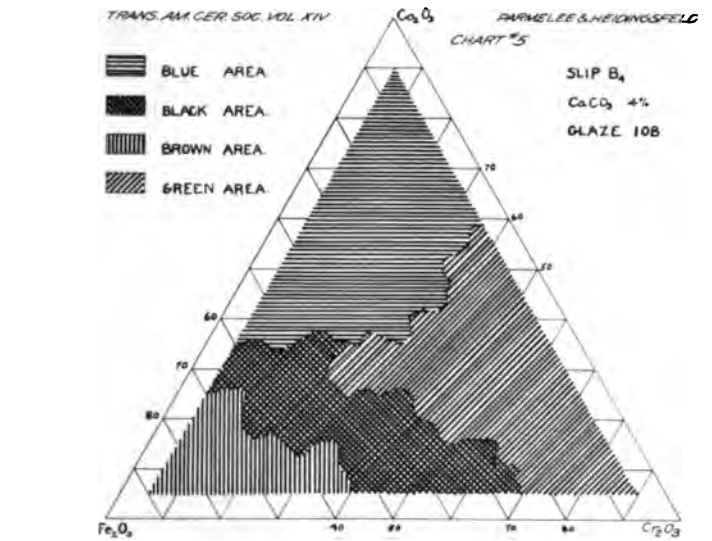

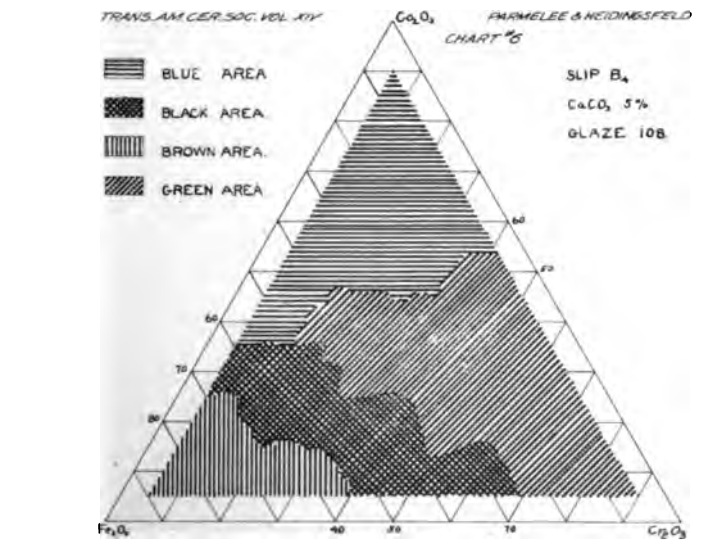

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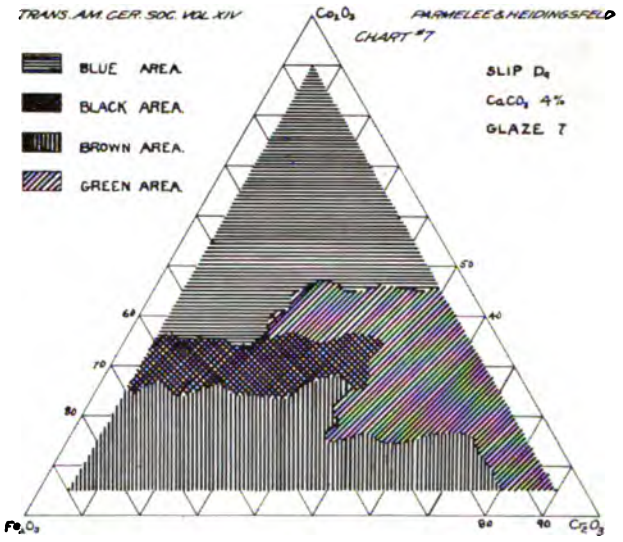

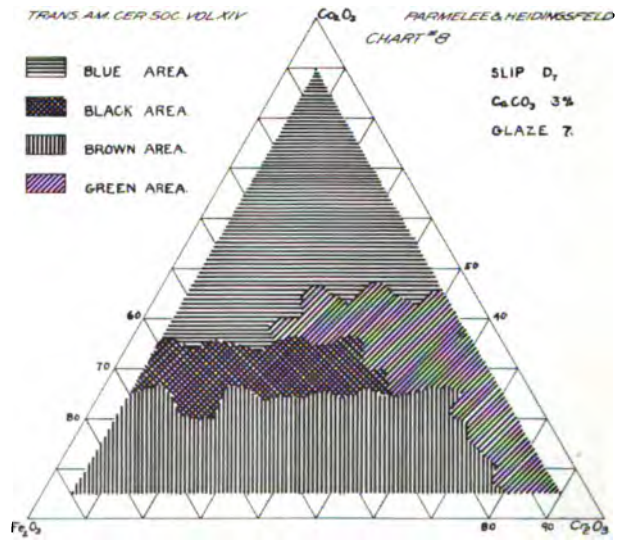

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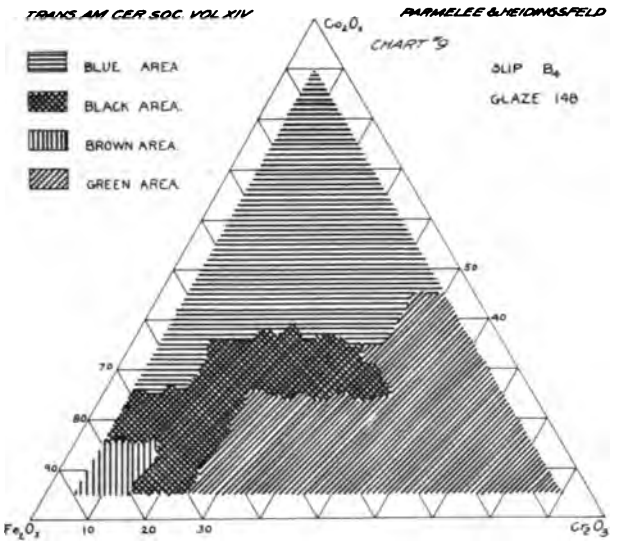

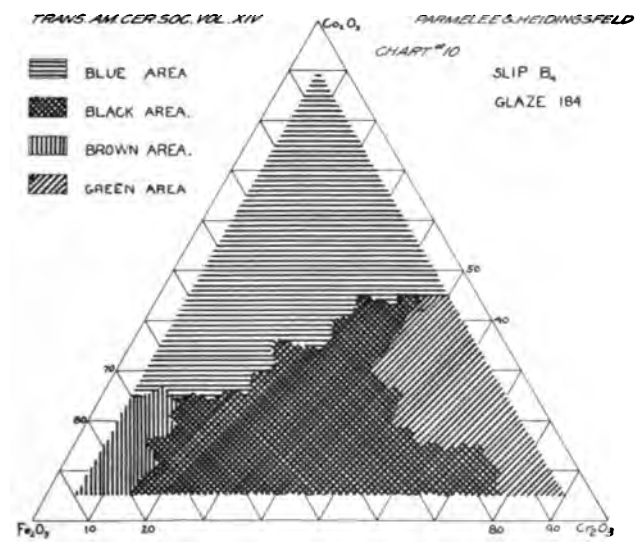

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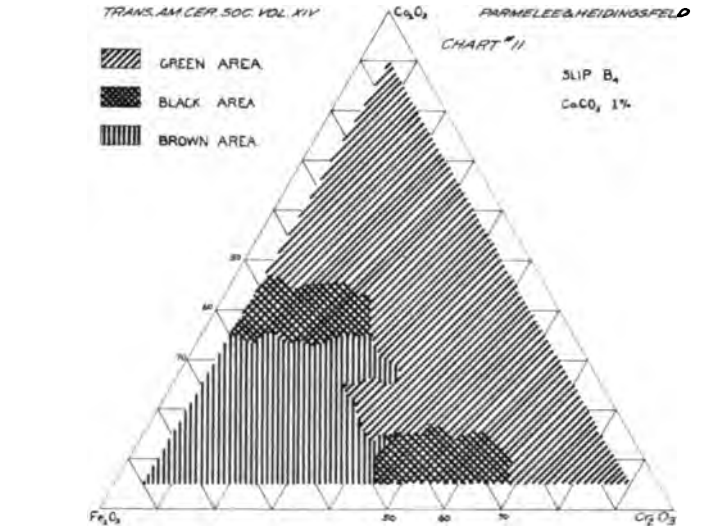

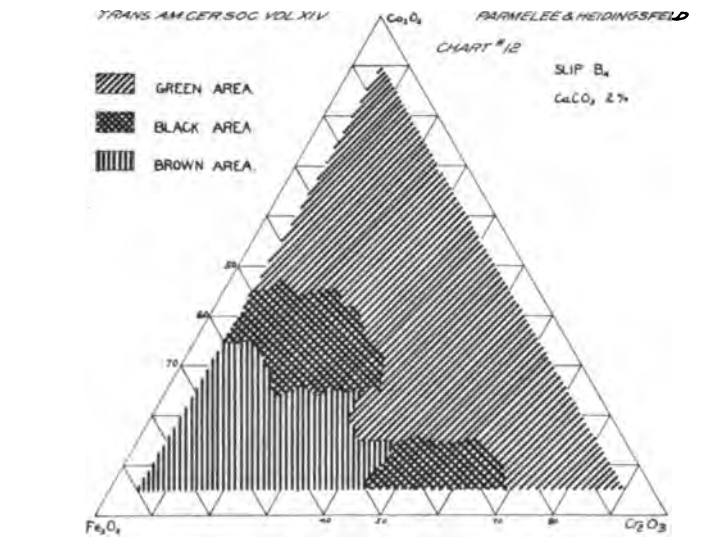

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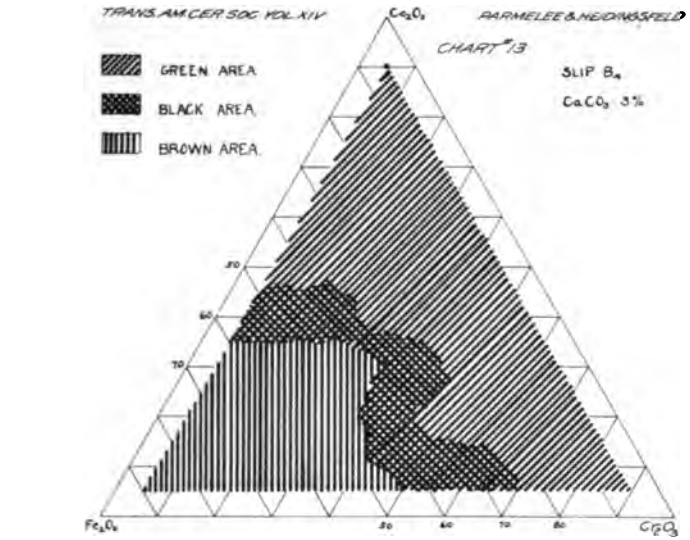

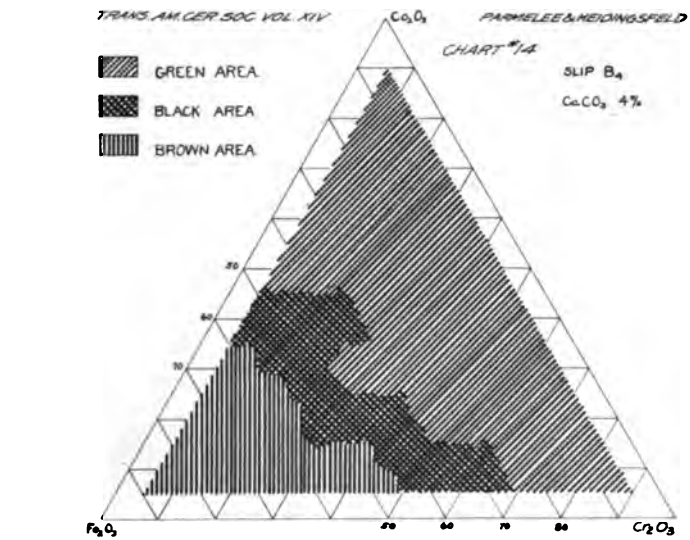

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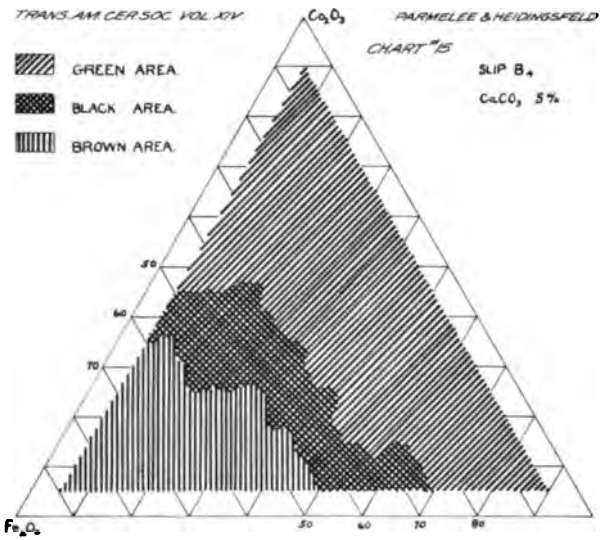

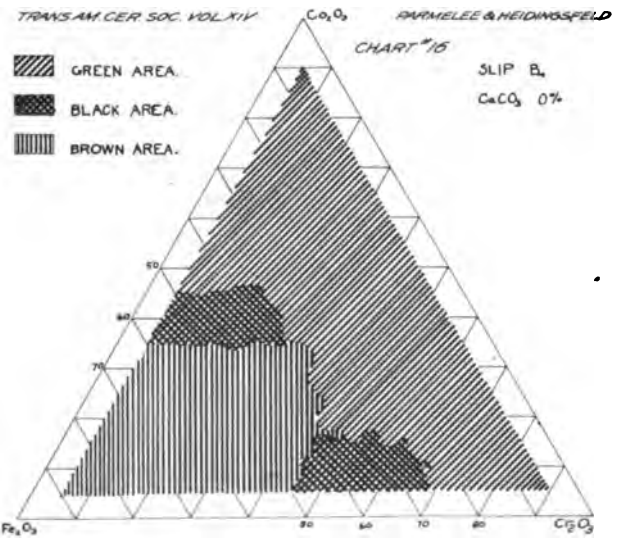

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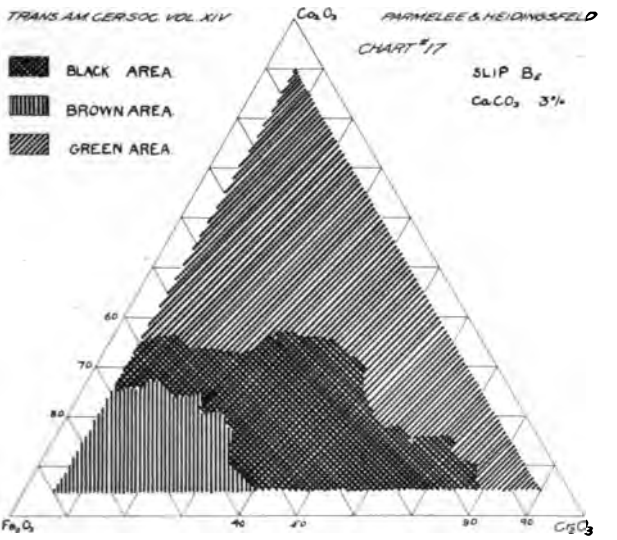

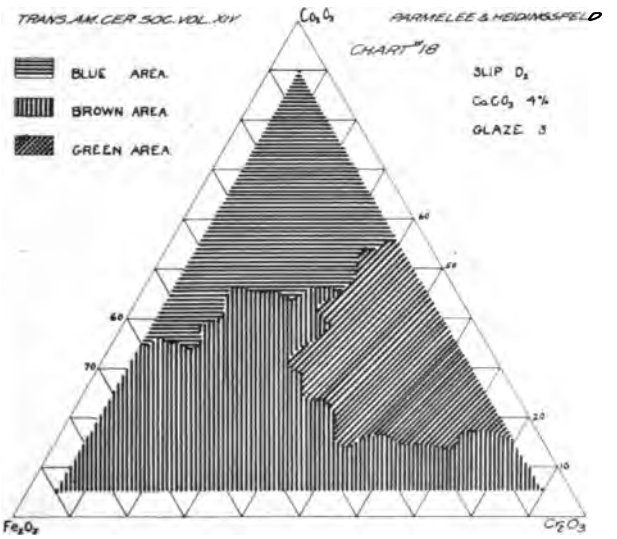

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THE CLAYS AND CLAY INDUSTRIES OF ARGENTINA.

By JAUN HOURSOURIPÉ, Bucyrus, O.

Argentina, as a country, is yet very new, and although in some respects it is highly developed, it must be said that the clay industry is in its infancy. In order to give a better idea to the reader in this limited space, the discussion may be divided into three different parts, as follows: the market; the clays; the processes of manufacture.

THE MARKET.

It is rather fortunate that Argentinians have inherited from their motherland, Spain, the custom of building their dwellings in brick masonry. They regard the home as something almost everlasting, and, consequently, want to see that their houses are built of a solid, substantial material, which cannot be affected by the weather or time.

Until quite a few years ago, Argentina was known to foreigners as the land where the city of Buenos Aires was located. To-day, even if not very well known, it is regarded as a country which produces enormous crops of wheat and corn, great quantities of wool, and as an important factor in the meat markets of the world; in other words, it is a country of great wealth.

Buenos Aires, the capital of Argentina, wisely protected by its municipality against the dangerous and temporary timber construction, is an up-to-date city in every respect. In importance, it is the fourth city of America, coming after Philadelphia, with a population of 1,350,000. All the houses are built of brick, with the walls plastered; cement is beginning to be used and stone is practically unknown in building construction.

The area of paved streets in Buenos Aires is 7,290,861.79 square meters, distributed as follows:

	Square meters
Wood	542,393.42
Trinidad asphaltum	302,717.03
Granite, with basis of sand	1,571,122.41
Granite, with basis of concrete	3,290,782.86
Granite, with basis of Portland cement	541,668.88
Natural asphaltum	28,631.04
Macadam	262,506,10
Stone	650,334.93
Total	7,290,861.79

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The paving brick has not had, as yet, an opportunity to show its merits, but this must not be taken as signifying that Argentinians are prejudiced against this kind of pavement. The reason is one of circumstances, for, up to this time, suitable clays for vitrified products have not been found near the city.

The materials of which the sewage system of the city is built are as indicated below:

	Meters
Masonry pipes	91,983
Vitrified products (imported)	303,744
Vitrified products (domestic manufacture)	2,985
Cast iron	150,652
Total	549,364

At present there are under construction improvements in the water system of the city at a cost of $80,000,000.

Rosario, on the Parana river, several hundred miles in the interior, has more than 200,000 inhabitants, coming second to the capital, and has a harbor available for large ocean vessels. It is a city that is growing at gigantic strides, offering an excellent market for the clay industry.

Other cities of importance in this country of Latin-America are:

La Plata (founded in 1882) with a population of	102,000
Avellaneda with a population of	105,000
Tucumán with a population o	105,000
Córdoba with a population of	100,000
Mendoza with a population of	80,000
Paraná with a population of	50,000
Bahia Blanca with a population of	75,000

The last is a city of great future, being the wool and crops market of Patagonia or Southern Argentina.

Scores of smaller towns of 25,000 to 30,000 are to be found in Argentina, but as the purpose of this paper is not to give details, but a general idea, their names are here omitted.

Summarizing, it can be said: That the market is excellent for clay products, for there is no competition from wood or stone.

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Cement is still a relatively new product and is just beginning to be manufactured. Clay is practically the undisputed building material.

THE CLAYS.

In the province of Córdoba (central part of the country) is located the *sierra* of the same name. The main bulk of the Sierra de Córdoba consists of granite, slate, granular calcareous material, and sand. All this material is covered by sediments of argillaceous material; in some places this clay deposit has a thickness of about 1000 meters, constituting what is called in Argentina the *Terreno pompeano*. In all these deposits stratification is to be noticed. Interposed in the strata are to be found layers of sandy material.

Almost all the clays, with the exception, maybe, of some superficial ones, contain carbonate of calcium, the amount of this substance increasing gradually with the depth. Especially rich in lime are the lower layers in the section of the *sierra* called La Punilla, this being undoubtedly a case of water sedimentation.

Volcanic ash participates in the formation of the deposits in the sierra and appears to be in two layers of not a great thickness. One of these layers runs through the upper part and has a white color, while the other, of a greenish gray color, runs through the lower part.

Sodium chloride, sodium sulphate, magnesium sulphate, etc., appears in the surface of the near-by valleys after rains and are present in a great many cases in the waters of wells. This proves that the *Terreno pompeanos* are impregnated with these salts, and that they are absent in the places where they have been washed away by rains, the streams of rivers, and by subterraneous waters. In the depressions without an outlet for the waters, these salts have been concentrated.

The material of which the *Terreno pompeano* is constituted has its origin in the erosion of the rocks which form the *sierra*, and among them the most important are the sandy deposits that in *prepampean* times have covered a great part of the sierra and have been carried away by the waters towards the depressions of the near-by valleys. Andesite with calcareous tufa, traver-

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tine, etc., have contributed equally to its composition, and likewise, although locally, the volcanic ashes. Finally, the granite and slate, which constitute the main bulk of the central part of the *sierra*, attacked by erosion, have given and continue to give material, which is taken away to the near-by valleys.

The amount of kaolin in the Sierra de Córdoba is very small. In the year 1880, a deposit containing a clay of high grade, probably a ball clay, was discovered in the place called Piedras Grandes, near San Antonio, in the section LaPunilla, and as a consequence a German company started a pottery. This clay deposit was soon exhausted and the enterprise proved to be a failure.

At present there is a place where some china clay is found. This clay is washed and put on the market. The quantity is so exceedingly small that it can hardly be claimed that such a mineral has an existence in the country.

Other minerals of importance in the province of Córdoba are: marble, granite, gneiss, serpentine and asbestos, basalt, andesite, feldspar, quartz, mica, beryl, fluorspar, talc, volcanic ash, common salt.

In the provinces of San Juan and Mendoza (Andes Section), a great many deposits of clay have been found. The largest deposit is located in the transversal valley of the Jachal river, between the Cerro Alumbre and the Cerro Blanco, near Rodeo. This clay has a yellow color and in places greenish, containing a great many fresh water fossils, which is an evidence that this deposit has been left by a lake that existed there at some earlier geologic time. A similar clay is to be found in Barrealito, near Iglesia, but somewhat more sandy. The thickness of these clay deposits is about 30 meters. The soil of the region called Angaco Norte, near the province of San Juan and the Cerro Piede Palo, is made up of the same kind of clay.

Besides these deposits there are a great many others in the Cordillera and Precordillera. The real amount and value of these would be hard to tell at present, due to the undeveloped condition of the country.

Petroleum is known already to exist in several places. The most important sources are at: Covunco and Picun-Leafu

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in the territory of Chubut; Oran, province of Salta; San Pedro, province of Jujuy; etc. Some coal has been found at Las Higveras, province of Mendoza.

Other important minerals in the Andes section are: borates, bismuth, copper, galena, gold, lead, mica, common salt, silver, tin, wolfram, etc.

The clays used in Argentina for making ordinary building brick are alluvial deposits, or any kind of mud regardless of its composition.

MANUFACTURE.

Winning.—The process of winning the clay may not be a very modern one, but it is rather interesting to see. The clay is dug from the ground with shovels by gangs of men paid from $1.50 to $1.75 per day. The transportation is done by rather large wagons that dump backwards, drawn by ox-teams at a very slow rate. Naturally there are some exceptions to the rule, but this is the general way of doing things.

Mixing.—The mixing is done by no patented pug mill. The clay from the wagons is dumped into a round soak pit, and when the proper amount of material has been collected, the water is poured in and a troop of fifty or so mares made to trot freely in the pit until the mud has obtained a consistency to suit the brickmaker. At this stage of the mixing, a quantity of manure is introduced into the pit with the purpose of making the mud hold together better in the body of the brick during its shaping.

Shaping.—The shaping is accomplished in ordinary wooden moulds, which are the same as those used in this country in yards where the soft-mud, hand-made brick is produced.

Drying.—The drying is done entirely in the open air, this method having the advantage of economy of fuel against the many disadvantages, familiar to the reader, that affect the system of drying.

There is a rainy season that begins as a rule the first days of May and lasts until the first of August. During this period a great many brickyards have to discontinue their work.

Burning.—The bricks are burned in square, up-draft kilns. The fuel used is almost entirely wood, and the use of coal is something that cannot satisfy the mind of the brick-maker, for he is

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not familiar with this material. All the coal used in Argentina is imported from England.

In the northern part of the country are to be found immense areas covered with forest. The best wood is to be found in the provinces of Salta, Jujuy, Santiago, del Estero, and the territories of Chaco and Formosa, especially in these two latter places. In the three former places no work whatever has been done, due in part to the lack of adequate means of transportation, and in part to the circumstance that those forest lands furnish good pastures for the cattle and are very much used for that purpose.

The wood obtained from the places above mentioned is of excellent quality. The kinds of wood that predominate are: *quebracho blanco*, *quebracho colorado*, *urunday*, *ibirapitamini*, *ñandubay*, *palo-santo*, etc. Of late great activities have been displayed in the development of Chaco and Formosa, and to such an extent that the value of the land has been doubled in the last ten years.

The transportation is done almost altogether by water, and the main conduits are: the Bajo Paraná, Paraguay and Vermejo rivers. A few railroads go through that part of the country.

In the southern part of the country is another big forest section, which produces a much lower grade of wood, but still very good for fuel. This area includes the territories of La Pampa Central, Neuguen, Rio Negro, Chubut and Santa Cruz. This section, the same as the one already mentioned, is almost untouched. Here the transportation is done entirely by rail.

The northern part of the province of Santa Fe, the provinces of Entre Rios, Corrientes, and the territory of Misiones are also sections which have a bright future as wood producers.

As wood is a home product, it is preferred by burners to the imported and not so well-known material Weight by weight, coal is sold a little cheaper than wood (near the city of Buenos Aires); and as the calorific value of the former is higher than the latter, there is no doubt but that there coal has a great advantage over wood.

The bricks manufactured by the process above mentioned

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are extremely porous. They would certainly be a very undesirable material for building construction if it was not for the fact that the exterior of the houses are always plastered, a feature that tends to minimize this faulty structure to some degree.

Vitrified brick, sewer pipes, roofing tiles, etc., are not produced so far. The lime-silica brick has begun to be manufactured.

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A GLAZE IMITATION OF GRANITE.

By RALPH HEIDINGSFELD.

A cheap way of imitating granite has been one of the problems of the terra cotta industry. It was my idea to obtain a glaze which could be applied with one spray and which would contain the mottled effect which is so prevalent in granites. The fact that the black spots in a granite consist of biotite, hornblende, and other ferro-magnesian minerals first suggested to me that perhaps these minerals could be mixed in a glaze and give the granite effect with one spray, thus eliminating the necessity for spattering the black spots on the surface of the glaze.

My first experiment was to mix some biotite, ground to pass a 10 mesh sieve, in bright glazes:

0.2 ZnO 0.4 CaO 0.3 K_2O 0.1 MgO	**A.** 0.35 Al_2O_3 4.1 SiO_2	0.3 ZnO 0.1 CaO 0.3 K_2O 0.3 MgO	**B.** 0.35 Al_2O_3 4.1 SiO_2

0.4 K_2O 0.2 CaO 0.4 ZnO	**108.** 0.56 Al_2O_3 3.08 SiO_2

and in the semi-mattes:

0.1 MgO 0.1 BaO 0.4 K_2O 0.4 CaO	**184.** 0.56 Al_2O_3 3.08 SiO_2	0.1 MgO 0.2 BaO 0.4 K_2O 0.3 CaO	**185.** 0.56 Al_2O_3 3.08 SiO_2

These were burned in a test kiln to cone 6 (18-hour burn).

I found in all cases that the biotite gave a brownish black spot somewhat fused at the edges, and that crazing resulted in the case of Glaze A. Crazing in these two glazes was the reverse of this when the biotite was omitted.

I next tried successively hornblende, tourmaline, graphite, garnet, franklinite, an altered biotite found mixed with the sand in New Jersey, and specular iron ore from Ishpeming, Michigan, to obtain a black spot, and muscovite to obtain a shiny white spot.

Hornblende fused to a jet black spot, but it would be impracticable to use this commercially because it settles so rapidly in the glaze. I tried dusting it on the body and spraying the

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glaze over it, but this also proved impracticable because it was blown off by the sprayer.

Tourmaline fused to a dull brown spot, but its use is also impracticable because of the rapidity with which it settles.

Graphite gave a black speck but in nearly all cases caused crazing.

Garnet fused somewhat to a jet black lump but was too refractory. It also settled too rapidly for practicable use.

Muscovite remained unaltered and retained its luster in semi-matte glazes.

Franklinite proved itself too refractory.

Damourite, or the altered biotite, from New Jersey gave an excellent effect. The spots ranged from a yellow to a dark brown, giving the appearance of a light granite. It did not cause crazing in any instance.

The best effect was obtained with the specular iron ore. This gave a lustrous black spot, imparting to the glaze the spangled effect which one sees in a polished granite. This effect was seen best in glazes of the semi-matte texture. It also worked very effectively in glazes which were just a little too refractory for the temperature. The rough, shiny surface of these glazes looked exactly like semi-polished granite.

BODY, ENGOBE AND GLAZE FORMULA FOR IMITATION GRANITES.

A light brown small-specked granite imitating Westerly, R. I. granite:

Body: ½ Campbell's No. 33. ½ Edgar's No. 9.....	70%	Engobe: Crossley ball clay...	15%
		English china No. 7 clay.....	20%
Fine grog.....	30%	Golding flint.....	20%
		Golding spar.....	45%

Glaze: 0.4 K_2O, 0.2 CaO, 0.4 ZnO } 0.56 Al_2O_3 3.08 SiO_2

Add to the glaze 2½ per cent. of maurilite, which can be obtained in New Jersey by washing the sand found near South River, South Amboy, and Cape May. Finely ground biotite will give approximately the same result.

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For a yellowish brown, small-specked granite, imitating Westerly, R. I., granite:

Same body and engobe.

Glaze: 0.1 MgO, 0.2 BaO, 0.4 K_2O, 0.3 CaO } 0.56 Al_2O_3 3.08 SiO_2. $2^1/_2$% maurilite.

For a light gray granite imitating Barre, Vt., granite:

Same body and engobe.

Glaze: 0.4 K_2O, 0.2 CaO, 0.4 ZnO } 0.56 Al_2O_3 3.08 SiO_2. $2^1/_2$% specular iron ore.

Dark granite, highly polished:

Same body and engobe.

Glaze: 0.1 MgO, 0.2 BaO, 0.4 K_2O, 0.3 CaO } 0.5 Al_2O_3 3.5 SiO_2. 3% specular iron ore.

For a semi-polished light granite:

Same body and engobe.

Glaze: 0.1 MgO, 0.1 BaO, 0.4 K_2O, 0.4 CaO } 0.65 Al_2O_3 5.85 SiO_2. $2^1/_2$% specular iron ore.

For a dull gray granite:

No engobe, same body.

Glaze: 0.5 K_2O 2.5 Al_2O_3, 0.5 MgO 0.05 Fe_2O_3 } 9.86 SiO_2. 3% specular iron ore.

DISCUSSION.

Mr. Simcoe: I would like to go on record as questioning the proposition of getting a spot from graphite. A paper I will read later will show that apparently we do not get any speck at all from graphite. I find that graphite burns out from a glaze, and also from a biscuit piece. I see no reason why it should not burn out; it is carbon.

Mr. Stephani: I should imagine the cone they were burned to would have some effect on the graphite. I would like to ask to what heat these samples were burned?

Mr. Heidingsfeld: Cone six.

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Mr. Stephani: I am in the terra cotta business and have had considerable trouble with granites at times to match them. We get stones, the sample of the stone being three or four inches square, and will match them, or that particular piece of stone, and get it to the job and the granite itself varies a good bit and there is often a kick about the terra cotta not matching a certain other piece of stone at the building. I merely mention this fact to show how variation in natural stone occurs and yet how some architects will insist on the terra cotta itself being absolutely uniform in color. This is not so difficult in one system of spotting, but on some granites where three or even four spottings are necessary to match the stone, chance enters so largely into the proposition that results are questionable. This paper is a very valuable paper for anybody in the terra cotta line trying to imitate granite. These results match the black and white granite, which is known as Mt. Airy granite. Now the proposition comes up of working out the color of the Deer Island granite; that is, a granite with the brown spots, some black, some yellow and white in it. I don't know whether any work has been done along these lines or not. In applying two or three different kinds of specks, the result depends upon the man putting it on to get the same number of specks on all pieces. If we could get the brown specks in the application of the glaze alone and incorporate the brown and black specks in glaze mix, it would be a long step towards imitating granite.

Mr. Simcoe: I am frank to say in connection with my point, that as Mr. Stephani has said, the temperature may have something to do with it. You say that those examples were burned at cone 6. Now, in my experimenting with the material I burned at cone 3, 6, 8, and 12, and at cone 3 the graphite burned out. So that is burning out lower than the point named.

Mr. Stephani: I have not done much work with graphite to know just how it would act; however, it seems to me that you would get some specks in it on account of its impurities.

Mr. Simcoe: That is a good point. In that connection, I got hold of some graphite that was impure and I got some specks, and as it was old and had been lying around for some time, I took it up with the manufacturer and got what he claimed was

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an absolutely pure sample of graphite, and all my work was done with this pure material.

Mr. Stephani: I burned some lead crucibles for the crucible steel industry and in that burning the graphite left a black spot.

NOTE PREPARED AFTER READING ABOVE REMARKS.

Mr. Heidingsfeld: In my paper I stated that I obtained a brown spot with tourmaline. I also succeeded in obtaining a yellow to a dark brown with damourite. By mixing specular iron ore and damourite, a granite could be obtained with spots ranging from a yellow to black. Thus by the use of proper minerals any combination desired could be obtained.

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THE RELATIONS BETWEEN MANUFACTURE AND PROPERTIES OF REFRACTORY CLAY WARES.

By W. STOUT, Columbus, Ohio.

The demands made on refractory clay wares vary in character with the use to which the wares were put. In this paper I wish to discuss the relations of character of clay and method of manufacture to the ability of the finished wares to withstand various stresses when in use.

HEAT RESISTING WARE.

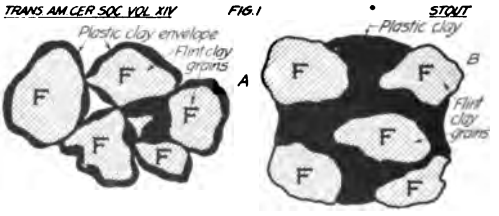
In this section I wish to discuss the manufacture of ware for use where high heat is the principal stress to be undergone.

The Clays to be Used.—The best grade of fire clay obtainable should be used. The clay should stand a heat test of cone 33 in a Deville furnace or under reducing conditions. The basic fluxes should not run over four per cent. and preferably much lower. The acid fluxes should be four per cent. or under and total fluxes under six per cent. The alkali and alkaline earth bases should not total over two per cent.

Calcined flint clay of same quality to hold up shrinkage where this is too great should be used.

The best grade of plastic clays, or better yet, a well weathered semi-flint should be used. The plastic ingredient should be kept as low as possible, for in most refractory ware this is the weak part of the mixture. Semi-flint clays soften much earlier than flint, and plastic clays much earlier than semi-flint, where all stand about the same cone test. In no case should the plastic ingredient be such that it will soften or vitrify at near the temperature to which the ware will be subjected. It should be well above this temperature as it fatigues quickly.

Proportioning the Clays.—The amount of plastic clay should be kept very low. For example, see Fig. 1, A. Here the



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flint clay grains have a thin coating of plastic clay, just enough to cement the grains at the points of contact and fill small voids between the flint grains. This brick will have approximately the heat-resisting qualities of the flint clay. In Fig. 1, B the grains of flint clay practically float in bond clay and the brick will have only about the heat-resisting quality of the plastic clay. Excess of plastic clay is one of the most common faults found in this grade of ware. Keep the plastic clay so low it will just or not quite fill the voids made by grains of flint clay, never more than this.

Grinding of Clay.—The grinding should be done in a wet pan to get the full plasticity of bonding clay and to get the maximum number of different sizes of grains. Then the smaller grains of flint clay will fill the voids made by the larger grains, and a better interlocking of grains is obtained. Also, there will be less voids to be filled with plastic clay.

Moulding.—This should be done by hand as the structure of ware obtained is much better than where the ware is made by a machine. Do not use sand in moulding, as sand-cracks are detrimental to the strength of the brick and give a point of attack for corrosive gases or slags. The mud should be made as stiff as it can be moulded.

Drying.—This should be done by methods such that the entire brick is brought to a leathery condition at the same time. Most fire brick are dried on floors that are too hot. The outside is in the right condition or temper, the inside is too soft. When the brick are pressed with this wet core, strains are produced on further drying which later may cause cracking of the brick.

Pressing.—Brick should be pressed when they are in a tough leathery temper, or consistency.

Burning.—Coal-fired brick have the best structure. At every baiting of the fire the brick are cooled somewhat. This heating and cooling effect causes an annealing or firmer setting of the grains with consequently a more complete bonding of the mass. Gas-fired brick are not subjected to this heating and cooling or annealing effect, and so are generally very punky. Gas is used by some yards because the iron is not reduced or flashed and thus it gives a much lighter colored brick.

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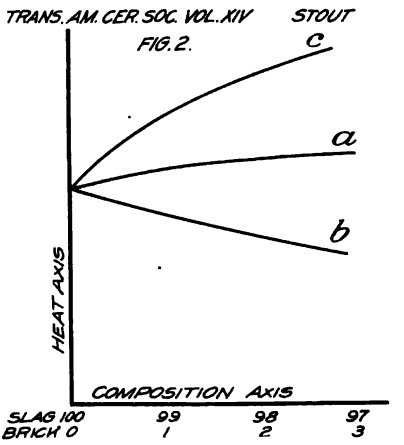
All high-grade refractory ware should be burned at cones 13 to 15. At cone 13 the last water shrinkage is gone, and there is no need of going beyond cone 15. A very small per cent. of the brick on the market are burned to this temperature and so will shrink when used and often cause trouble. Even if the brick are not subjected to this temperature in use, they soon fatigue and thus shrink.

WARE TO WITHSTAND THE ACTION OF SLAGS.

The ability to withstand the action of slags depends on both the composition of the brick and that of the slag and is a problem of physical chemistry. Take the action of the furnace slag on the fire brick lining of a blast furnace. When one unit of slag is formed from the different acid and basic elements about 150 calories of heat are set free. So when the slag attacks the brick lining, heat is given off and also the fusion point of the resultant slag is either lower or higher than that of the original slag. We have three possible cases (see Fig. 2).



I. When x parts of brick plus y parts of slag go into solution to form one unit of slag and the fusion curve is lowered as along b, then the extra 150 calories of heat given up tend to cause additional fusion. Solution in this case will be rapid.

II. When x parts of brick plus y parts of slag go into solu-

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tion to form one unit of slag and the fusion curve is raised as along *a*, then this extra 150 calories of heat will be used up to raise the slag to its fusion point but will not tend to promote more fusion.

III. When *x* parts of brick plus *y* parts of slag go into solution to form one unit of slag, but the parts from the brick greatly elevate the fusion point so that the 150 calories of heat will not raise the body to its fusion point, additional heat from an outside source is needed and fusion will be very slow.

Bricks should be chosen of such a composition as to work against a definite slag, so that when the slag tends to take it into solution the fusion point of the resultant slag will be the highest possible. Special attention should be paid to the composition of brick for each separate slag.

Brick for resistance to slag action should also be dense to keep the area of surface exposed at a minimum.

But little attention has been paid by brick people to resistance of brick to slag action.

ABRASION AND DIFFERENTIAL HEAT TREATMENT.

Here the brick should be dense and hard, but not vitrified. If for abrasion alone, then vitrification would be desirable; but under differential heat treatment any vitrified material will check or pluck. Here, if ever the bond clay is vitrified, it soon goes down. The best brick are those made from a hard flint or calcined flint with enough bond clay to fill the voids, ground very fine, pressed hard, and burned to a good bond but not vitrified or with any part vitrified. Such a brick stands good abrasion tests and will not check when subjected to differential heat treatment.

Highly silicious brick are of little value. They withstand the abrasion but soon go down under heat changes due to the expansion changes caused by quartz changing to tridymite.

SOME GOOD CLAYS.

Location.—The deposits of clay best suited for high-grade refractory ware are confined principally to the Pottsville and lower Allegheny formations of the carboniferous system. Those best developed are:

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1. Allegheny series, Brookville formation in the Clearfield district, Pa.

2. Allegheny series, Brookville formation in the Clarion County district, Pa.

3. Pottsville series, Mt. Savage formation in the Mt. Savage District, Md.

4. Pottsville series, Sharon formation in the Olive Hill, Ky., and Sciotoville, Ohio, districts.

These clays approach the kaolinitic formula quite closely and have the true flint-like nature which is necessary for high-grade refractory ware.

Analyses.—Analyses of brick from three best clay fields showing about what should be expected for high-grade ware:

	Clarion Co.	Olive Hill	Clearfield
SiO_2	53.65	54.40	51.87
Al_2O_3	42.31	41.19	43.21
FeO	0.69	1.35	1.86
CuO	0.27	0.08	0.42
MgO	0.26	0.32	0.35
K_2O	0.87	0.23	0.31
Na_2O	0.62	0.13	0.19
P_2O_5	trace	0.11	0.04
TiO_2	1.46	1.82	1.86
	100.13	99.63	100.11
Basic fluxes	2.71	2.11	3.13
Acid "	1.46	1.93	1.90
Total "	4.17	4.04	5.03
$\frac{SiO_2}{Al_2O_3}$	1.27	1.32	1.20
Cone	34–35	34–35	33–34

Theory of the Formation of These Clays.—These clays seem to have been of chemical origin. They seem to be chemical precipitates formed in the open waters of the swamps during the coal measure period. The silica and alumina derived from the mineral residue of the dead plants by the action of the organic acids, produced in plant decay, were carried as soluble compounds

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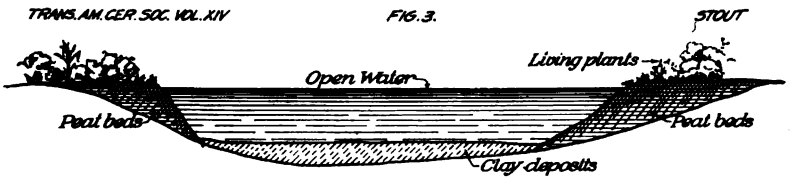
to the open waters where the compounds were broken up with a uniting of the silica, alumina and water to form kaolinite in an amorphous form. My idea of the formation of the fire clay beds is illustrated in Fig. 3.



Facts to Support this Theory.—The analyses of ash from pure coal seams approach the right amounts of silica and alumina very closely. The best clays have but little, if any, coal above them. These deposits show a sudden change from floor materials, such as sand-rocks or shales, to a fine quality of clay. Some deposits show no plant markings. Some show plant markings in upper part only, as if these beds had finally grown out over them. The changes from flint to semi-flint could be from different composition of swamp waters. The best clays are confined to pocket formations. There are also many other points in favor of this theory that I shall not discuss at this time.

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THE USE OF A THERMO-COUPLE PYROMETER IN A PAVING BRICK PLANT.

By DWIGHT E. HUMPHREY, Cleveland, O.

Introduction.—High temperature measurement has always been a serious problem with the clay working industries. It has received a great deal of attention from a technical standpoint, but, until the last few years, the maker of paving brick has been too busy with the more fundamental problems of manufacture to bother himself with refined methods of measuring temperature. As paving brick yards grow older and more numerous, competition becomes keen and more attention is given to the smaller details which cheapen the cost of manufacture and assist in the production of a better product.

In an attempt to meet the demand for a practical means of measuring high temperature, instrument makers have offered many different makes of thermo-couple pyrometers. A large number of the Ohio brickyards have lately tried a pyrometer. In many cases the results have been unsatisfactory. It seemed to me an account of The Deckman-Duty Brick Company's experience with a thermo-couple pyrometer might be of value to some who are about to purchase an instrument.

Reasons for Failure of Pyrometers.—No matter how much a burner prides himself on his ability to judge temperature by looking through a peep hole, it is not uncommon (after he has burned a bad kiln) to hear him wish for something that will tell him just exactly what temperature he is carrying. Along comes the pyrometer salesman with a nickel-plated instrument and a nice line of talk. It seems to the man, inexperienced with pyrometers, that the often-wished-for something to determine temperature has been produced. He buys a pyrometer with the expectation that as soon as the magic wand (the thermo-couple) is placed in the crown of his kilns all troubles will forever vanish. The pyrometer is delicate and sometimes it gets out of order. It fails to produce all number one ware and to cut the coal bill in two. After burning a few kilns by the pyrometer, the burner generally gives up in disgust. He falls back on the old reliable eye peep-hole method with the firm conviction that he can tell

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heat better than all the pyrometers in the world. Often, after such an experience, the pyrometer is discarded as an expensive and impracticable equipment for a brickyard.

There are three reasons why pyrometers have been unsatisfactory in so many cases. First, the purchasers have expected too much of them. Second, the instruments are not rugged enough to stand unskilled, careless use. Third, pyrometer makers have not properly designed their instruments for the class of work in which they are to be used. They make one standard instrument, which they expect will meet the requirement of the steel, glass, and clay industries. I suppose the pyrometer must remain in the unsatisfactory stage of development while the makers learn how to construct their instruments and the users learn how to use them.

A Successful Instrument.—After several trials and considerable expense on the part of the company with which I am connected, a type of instrument has been evolved which, if properly used, will give good results in the burning of shale paving brick. The company's experience with pyrometers began five years ago when they purchased a delicate indicating instrument of the thermo-couple type, and wired it to couples placed in the crown of six kilns. The outfit was so delicate and the instructions for installing so indefinite that it remained in service for only a short time. Several time-temperature curves were plotted from the temperature readings, but no practical conclusions could be drawn from so little data.

Two years ago, the company decided to try another pyrometer, this time with a determination to secure the equipment most suitable for its conditions, and then to determine whether such an equipment was worth maintaining. Each kiln was provided with an eighteen-inch platinum-iridium couple encased in a heavy protecting tube. To the sides of the kilns were attached poles over which the wires ran to the automatic switchboard and instrument in the building occupied by the burners. The automatic switchboard was so designed that any ten of the fifteen kilns may be automatically switched on the instrument one at a time while the temperature is being recorded. Never more than ten of the fifteen kilns are being

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burned at once. So this pyrometer serves to record the burns on all the kilns. The instrument makes its records on one strip of paper about seven and one-half inches wide. A record of one kiln is made every minute. So if ten kilns are recorded, the temperature of each one is taken every ten minutes. The record is made by an electric spark, which punctures the paper at the time and temperature indicated by the needle. The sparking device, paper shifter, and automatic switchboard are operated by an electric clock which hangs on the wall beside the instrument. This instrument was built according to our wishes by The Price Electric Co., of Cleveland. We found it necessary to make several alterations before an arrangement was secured which plainly and successfully registered ten kilns at the same time. Such an instrument is necessarily complicated and must be cared for by an intelligent and competent man.

Thermo-couples.—We have tried several kinds of thermo-couples. Thus far we find the rare metal couples most satisfactory for our use. A nickel-iron couple which we tried gave good results. It lasted for seven or eight burns, and it seemed to maintain its power to generate electricity better than platinum couples. The platinum platinum-iridium couples which we have been using rapidly lose their ability to generate electricity during the first two or three burns. After they have been used a few times, the electromotive force generated for a certain temperature does not apparently change very much. Some attribute this change to crystallization, and others think it is due to volatilization of the iridium alloyed with the platinum. I have seen bright metallic crystals hanging from the inside of a fire clay couple-tube that came from a glass furnace. Whatever the cause of the drop in electromotive force, the result is the same as far as practical service is concerned. The pyrometer registers a lower temperature after the couple has been used several burns. Beside any change which may occur in the electricity generated by a couple, the temperature indicated is affected by a change in temperature of the cold terminals of the couple. A rise in the temperature of the armature of the instrument increases the resistance and also changes the temperature indicated.

Advantages of a Pyrometer.—There are so many condi-

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tions which affect the temperature indication of a thermo-couple pyrometer that it is impractical to attempt to instal an instrument so that it will indicate actual temperatures. A pyrometer is of value on a brickyard because it indicates temperature change. I have never seen an instrument which, in my opinion, indicated the correct temperature. We believe our pyrometer is accurate enough to indicate the temperature of safe oxidation of our brick. It also acts as a danger signal when the temperature rises too high during vitrification.

After water smoking, the temperature is rapidly raised until the pyrometer indicates from fifteen to sixteen hundred degrees Fahrenheit in the crown of the kilns. The burner endeavors to maintain this temperature until the kiln is at a bright red heat to the bottom, or as the burner expresses it, "until the kiln has cleared up." He then increases the temperature, watching the pyrometer and taking settle or shrinkage readings with a rod through the crown of the kiln. As soon as the kiln begins to settle at its usual rate, he is assured the temperature indicated by the pyrometer is the one which should be carried until the kiln has its normal settle. If the pyrometer indicates a rapid rise in temperature, or a higher temperature than is generally carried during vitrification, the burner must proceed with caution until he is sure there is no danger of over-burning the kiln.

A recording pyrometer has the advantage of eliminating personal prejudice and mistakes. It makes a continuous record, which may be kept as reference when the kiln is drawn. If the burn is a bad one and no records have been kept, the cause of the trouble is generally put on the other fellows. If settle and pyrometer records are available, the cause of the bad ware may often be located. Since our pyrometer has been operating satisfactorily, there has been a gratifying increase in the percentage of the number one brick.

We believe our recording pyrometer has aided very much in increasing the percentage of number ones, and that the cost of maintenance is justified. At the same time, we recognize the fact that it was only by persistent, hard work that we reached the point where we could consider it a success. The instrument had to do its work for a considerable length of time without

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interruption before the burners placed any faith in it. Then, little by little, they came to know what help such an instrument could give them, and to recognize the faults which they must guard against if they are to make the most of a pyrometer.

DISCUSSION.

Mr. McClave: I was quite interested in the paper of Mr. Humphreys, as we use a thermo-couple pyrometer in one of our factories. I would just like to ask a few questions. Did you have any difficulty in getting your employees to follow your directions and instructions?

Mr. Humphrey: We did until we demonstrated that the pyrometer would show the danger points. By going over a record of a kiln which had been poorly oxidized or over-burned, we were generally able to show the reliability of the method of burning which we wanted the burners to follow.

Mr. McClave: I am glad to know that you secured an instrument that recorded correctly.

Mr. Richardson: I would like to ask Mr. Humphrey how long the platinum lasts?

Mr. Humphrey: It is my opinion that we got about ten or twelve burns out of the couples. We do not depend upon a couple for temperature indicated, so we use them until they break, or as long as they indicate at all. When the couple breaks, it can be taken to the manufacturer and reversed, making the hot end the cold end.

Mr. Richardson: How long are they?

Mr. Humphrey: Eighteen inches long.

Mr. Chairman: Are you able to turn your couples in and get value out of them?

Mr. Humphrey: We get a scrap platinum price for our old couples.

Prof. Parmelee: Have you ever noticed that suggestion made at the Pittsburg meeting, to the effect that, by putting one of these couples on an electric current which you could control, and by increasing the amount of current passing through, all crystallization could be taken out, and it would be just as good as in the beginning?

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Mr. Humphrey: I have never noticed it.

Prof. Parmelee: I have heard from electrical engineers that it is a good thing.

Mr. Humphrey: When we replace a couple it is always broken in two. The part exposed to the high temperature becomes very brittle.

Prof. Parmelee: You think it is due to the action of the carbon on your couples or firing that does it?

Mr. Humphrey: I stated in the paper that I did not know whether the brittleness was due to the crystallization or volatilization. All I know is that the couple becomes brittle and breaks. All our couples are enclosed in a $^3/_4''$ well-vitrified tube, which is supposed to be gas-proof. This in turn is enclosed in a heavy 3″ fire clay tube.

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PRODUCTION OF VITRIFIED BLACK AND CHOCOLATE FLOOR TILE.[1]

By Ross C. Purdy.

The compounding of vitrified encaustic tesseral have been discussed before.[2] At that time we were able to make vitrified cream and light buff tile but had failed to make the vitrified red, black and chocolate. We are still unable to make the vitrified red, but we have learned how to make the black and chocolate tiles that are vitreous.

The problem of making the so-called "clay colors" in vitrified bodies is worthy of as much attention as any that we now have before us, for the trade is using a very large quantity of these, but because they are not vitreous, hence unsanitary, it pays less for them than for the vitreous tiles. In this problem, then, we have an economic as well as a technical interest.

The finding of a way to make vitreous black and chocolate tile was made by members of the 1911 class in Ceramics, Ohio State University. Their report is as follows:

COLORING OF A STONEWARE CLAY.

By Harry Neal and C. T. Dun.

The problem was to produce a green, brown, black and a medium blue in a stoneware body at cone 6.

The work was divided up among the members of the group as follows: Longenecker, blue; Dun, brown and black; Neal, green.

GREEN (NEAL).

The class of 1910 found that no good greens were produced by adding stains containing chromium to a stoneware body. The problem then was to produce a green without chromium.

A search through the available literature failed to disclose a green stain which did not contain chromium. The only procedure left was to blend a blue and a yellow to produce the green.

Two stains were devised as follows:

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[1] Contribution from the Ceramic Engineering Laboratory of the Ohio State University.

[2] Trans. A. C. S., Vol. VII, p. 112.

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Green Stain No. 1.

CO_3O_4.....	20%
Fe_2O_3.....	80%

Green Stain No. 2.—This stain was produced by adding Fe_2O_3 to the blue stain given by Professor Purdy in the outline for the present study. The ratio of iron to cobalt was 2 : 1, the formula of the stain being:

Al_2O_3.....	64.5%
ZnO.....	6 5%
CO_3O_4.....	9.7%
Fe_2O_3.....	19.4%
	100.1%

These stains were calcined at cone 4 in a Caulkins muffle kiln, ground to pass 40 mesh, added to the bodies, the whole blunged in Bonnot ball mills for 3 hours, made into tiles by molding in the plastic state, and burned to cone 6 in about 30 hours.

DESCRIPTION OF TRIALS.

Stain No. 1.—Trials containing 5 per cent. stain: These trials were a dark brown on the exterior and a dark gray on the interior.

Trials containing 10 per cent. of stain: The color produced in this case was a good black.

Trials containing 15 per cent. of stain: The same as those containing 10 per cent. of stain.

Stain No. 2.—Trials containing 5 per cent. of stain: The color produced was a greenish gray.

Trials containing 10 per cent of stain: The color is a bluish green.

Trials containing 15 per cent., 20 per cent. and 25 per cent. of stain: These trials are all a good dark green with a very slight increase in the shade from 15 per cent. to 25 per cent.

CONCLUSIONS.

No greens were produced by the use of cobalt and iron alone.

Increase of stain over 15 per cent. produces no perceptible increase in coloring effect.

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[Note: These greens by the second stain would hardly be acceptable commercially although for some purpose where an olive-green can be used they would have value.—R. C. PURDY.]

BROWN AND BLACK (DUN).

To produce a brown and black with a stoneware body, the following stains were used:

Blue stain No. 8 (given in the outline):

Calcined Al_2O_3	80.0%
ZnO	8.0%
CoO	12.0%

Dark brown (Hainbach, p. 118):

200 parts Al_2O_3	56.2%
80 p rts Fe_2O_3	22.4%
76 parts chromic oxide	21.4%

Professor R. C. Purdy (Vol. VII., Trans. A. C. S.) produced a jet black with a bright red clay and 1.5 per cent. recovered manganese.

Bourry (p. 424) made black as follows: (1) a mixture of Fe_2O_3 and MnO_2; (2) a mixture of Fe_2O_3 and CoO.

Based upon the above references and others, the following series was made up:

No. of body	Per cent. clay	Per cent. Fe_2O_3	Per cent. MnO_2	Per cent. blue stain	Per cent. brown stain
1	99	0.5	0.5	..	..
2	98	1.0	1.0	..	..
3	84	3.0	3.0	10.0	..
4	80	5.0	5.0	10.0	..
5	70	10.0	10.0	10.0	..
6	65	10.0	15.9	10.0	..
8	95	..	..	..	5.0
9	90	..	..	..	10.0
10	80	..	..	..	20.0
11	70	..	..	..	30.0

The above bodies were fired to cone 6.

Results—Nos. 1 and 2 are brown, No. 2 being a good brown. Nos. 4 and 5 are good blacks. No. 5 shows a slight tendency to bloat, but this could be overcome by careful firing.

Nos. 8, 9, 10 and 11 may be called browns, but the color of

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these is more accurately described by the term chocolate. Nos. 10 and 11 are a good dark chocolate. All are well vitrified.

[Note by R. C. Purdy: Special attention is drawn to this series, for in my opinion we have here the only vitrified chocolate and blacks I have ever seen produced. I have seen such tile but never succeeded in making them in practice.]

CHECK EXPERIMENTS.

The results as above reported were of so much interest that we determined to check them. In these check experiments we used another fire clay, made new stains and made the trials by both the plastic and dry press methods. The results obtained by Neal and Dun were checked in every instance, the colors being practically the same by dry press as plastic. These check experiments were burned at cones 6 and 8 without loss of color.

DISCUSSION.

Mr. Will: I would like to raise one point; why chrome iron is not used? It is a great help to any one making brown and black stains or colors for ceramic purposes.

Mr. Purdy: Chrome iron is a very refractory substance that will not disseminate through the body at these heats. If you put chrome iron on a buff body you will get a speckled or gray as in bricks. Pulverized chrome iron will always give a gray on account of the buff and black showing side by side.

Mr. Will: Could not the chrome iron be ground fine enough so as to disseminate more readily?

Mr. Purdy: We have made a chrome iron stain by precipitation, getting it into pulp form, which gave a black; but while we can do it very nicely in the laboratory, on a factory scale it would be impracticable. If you want a solid color you have to get a stain that will completely hide the base.

Mr. Will: Some of the difficulties, encountered with chrome iron, as stated by Professor Purdy, can be eliminated by fine grinding, as is shown by the experience of tile manufacturers who use this material in making black or gray tile. As long as they use the ordinary technical grade the result is a fine speckle,

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but with the chrome iron ground to an impalpable powder they get a uniform color through the whole body.

Mr. Purdy: How about the black and gray?

Mr. Will: I was not referring to the colors obtainable, but rather to the advantages to be derived by using a finely ground chrome iron on account of its cheapness and stability.

Mr. Purdy: I want to say that by grinding chrome iron very fine we produced a silver-gray with a porcelain body as a base, but could not make a black by any such procedure.

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HIGH VOLTAGE INSULATORS AND HIGH POTENTIAL TESTING.

By E. T. MONTGOMERY, Pittsburgh, Pa.

At various times articles have appeared in our Transactions dealing with electrical porcelain and the testing of its dielectric strength, but notwithstanding the great importance of accuracy and uniformity in testing such materials, we have had no adequate discussion of high potential testing and the very many problems involved This lack of a standard test has already led to some confusion and a regrettable lack of uniformity and completeness in the reports of tests by several investigators in the field of ceramic engineering.

It is true that, even among electrical engineers, great accuracy in testing high tension insulating materials has not yet been attained, due to the great variability of the materials themselves, the difficulty of exactly controlling all the conditions of the test, and to our present lack of definite knowledge of the effect of all the factors involved.

The methods used and the results obtained by different investigators will undoubtedly vary between wide limits for some time to come, but we, as ceramic engineers, will be taking a great stride forward if we will learn to report all of the conditions of our tests, and, if possible, agree on some standard conditions and standard methods of testing.

This paper is, in fact, primarily a plea for standardization in high potential testing. While the ceramic engineer engaged in high voltage insulator investigations must necessarily call to his assistance the electrical engineer in making his tests, he should, himself, understand the essentials of those tests and the many factors leading to variations in results and hence the necessity of standardizing every possible detail.[1]

In the following discussion we will consider the problems

[1] While the writer has, for some time, felt the need of such a paper as here undertaken, he makes no pretense of being an electrical engineer, and, therefore, feels justified in presenting to the Society this paper, which is very largely an abstract of the very able discussion by Mr. A. B. Hendricks, Jr., before the A. I. E. E., February 14–16, 1911, on the subject "High-Tension Testing of Insulating Materials." It is in some places supplemented by the writer's own experience and that of others working in the same field of research.

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under two general divisions: 1. Apparatus used in testing. 2. Methods of testing.

We will, also, for the sake of simplicity, confine ourselves to the consideration of tests of ultimate dielectric strength only.

TESTING APPARATUS.

There are four main elements to be considered:

1. Alternating-current generator.
2. High-tension transformer.
3. Controlling apparatus.
4. Voltage measuring apparatus.

GENERATOR.

The generator should give an almost perfect sine wave form at all loads and power factors, and deliver high energy at the instant of rupture of the dielectric. It is necessary and sufficient that normal wave form and voltage be maintained up to complete failure of the test piece.

The critical final moments of the test are liable to be attended by high-frequency oscillations, which sometimes form a complete flash-over without leading to a dynamic arc. These oscillations have a negligible influence in the voltage of normal frequency, until a flash-over or momentary arc occurs, which may be attended by a sudden drop in voltage sufficient to prevent the formations of a continuous arc. It is at this point that the influence of the energy available becomes important, while previously it was of small consequence, the load being extremely small.

The best that can be done is to provide apparatus of capacity sufficient to supply the small charging and leakage current and the energy absorbed by dielectric hysteresis, with the closest possible regulation and minimum distortion of the wave form. By regulation is meant not only the voltage drop under continuous normal load, but particularly the drop at the first instant of short circuit, or the capacity for instantaneous short circuit current.

TRANSFORMER.

There has been a good deal of misapprehension in connection with the question of transformer capacity. It has been usual

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to specify a certain minimum kilowatt capacity for a given voltage, regardless of the other characteristics of the transformer, the engineer not realizing that such specifications are indefinite. It is not the rating stamped on the name plate that determines the energy in the discharge circuit, but the regulation, particularly as expressed by the impedance voltage, which has to be taken into account.

In the tests under consideration, the conditions are always at the extremes of small load or dead short circuit, excepting for an instant immediately preceding break-down, so the reactance is of chief importance.

In specifying transformer capacity, there should be expressed the kilowatt rating and the resistance and reactance voltages at full load, the kilowatt capacity being of interest only as a basis for determining regulation. There is, fortunately, no difficulty in obtaining very high kilowatt capacity with close regulation. The secret of the best designs of high tension testing transformers lies in the use of extremely massive cores, few turns in the winding, and reinforced insulation of the end turns. By this means, the poor regulation of the transformer and the great liability of the end turns to short circuit have been overcome.

It is good practice in the majority of laboratory tests to permanently ground the central point of high tension winding, and this is necessary if the voltage is measured by a voltmeter connected at the center of the high tension winding, as will be described later.

CONTROLLING APPARATUS.

In testing, the voltage must be varied through a wide range in a perfectly regular manner without breaks. To accomplish this, many different methods are in use, but the generator field control is the best for laboratory work. Where this method is not possible or practicable, an induction regulator may be used.

The field rheostat should be designed to vary the generator voltage in a perfectly continuous manner, or in very small steps, and the generator should always be operated at excitation as near normal as possible, for the sake of close regulation and good wave form.

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Either the generator or the low tension winding of the transformer should be wound with four parallel circuits. These may be connected in all necessary combinations by means of series parallel switches, cylinder controllers, or terminal board with movable links. Series parallel switches are simple and satisfactory, but the cylinder controller is least liable to lead to mistakes and is quickest in action, and therefore best. Four parallel circuits on the low tension side of the transformer have been found ample, and are more readily provided than on the generator. This gives 25 per cent., 50 per cent. and 100 per cent. of transformer voltage at normal generator voltage. The latter may be varied from 50 per cent to normal voltage, thus giving a range of 12½ per cent. to 100 per cent. transformer voltage.

VOLTAGE MEASURING APPARATUS.

SPARK GAP.

The most commonly used method of measuring the voltage applied to the insulator in testing is by means of the spark gap, using the curve between secondary or high-potential volts and air gap in inches, which has been authorized by the A. I. E. E. standardization rules. This method is, however, open to much criticism and liable to grave sources of error where accurate measurement of the applied voltage is required. It is close enough for commercial work, but other methods have been found more accurate for laboratory testing.

In the spark gap method of measurement, a voltmeter is placed across the primary circuit of the high potential transformer to record the voltage applied. The spark gap apparatus is then put in series with the secondary of the transformer, the needles adjusted at a definite gap, the voltage raised until the spark passes, and the maximum voltage noted just before the spark. This maximum voltage required to cause a discharge, in connection with the corresponding spark distance, gives a point on the curve between air gap distance and primary volts. This process is repeated until a sufficient number of points are obtained to plot the curve. Having thus found the curve between primary or low-tension volts and the spark gap in inches, and using the A. I. E. E. standard curve between secondary or high-tension volts and the spark gap in inches, a curve can be

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plotted between primary volts and secondary volts that will give the high potential voltage applied to the test piece for any recorded reading of the voltmeter in the primary circuit.

If the ratio of transformation between primary and secondary is accurately known for the whole range, it is then only necessary to check voltmeter readings against definite spark gap distances to see if the apparatus gives the standard A. I. E. E. curve.

The chief sources of error and the principal causes of variation in the spark gap method of measurement are as follows: difference in sharpness of the needle points; lack of perfect alignment of the needles; ionization of the air and change in atmospheric conditions; variation in the fundamental wave form; transient voltages; growth of charge in the circuit; disturbance from the resistance in series with the spark gap; and change of conditions between the time of spark gap calibration and actual test.

Sharpness of Needles.—This is best determined for accurate test purposes by means of a microscope with camera lucida attachment, so that each needle can be examined, measured for diameter, and an accurate outline drawing, both in plan and elevation, made. The voltage required to cause a spark to pass across a given gap is higher in the case of dull needles than in the case of sharp ones. It is also higher for needles out of perfect alignment.

Variation in Wave Form.—The effective voltage in causing a spark to pass is proportional to the maximum values of the potential wave. A flat top wave will give higher readings, and a peaked wave lower readings, in calibrating with the spark gap than will a normal sine wave.

Transient Voltages.—It is not, however, variation in wave of fundamental frequency that is the chief disturbing factor, but transient voltages generated by the variable conditions of the test circuit. In most cases these are of limited power and duration, and have negligible effect on the dielectric, unless high frequency oscillations across the spark gap are set up. Transient voltages may jump the spark gap without starting dynamic arcs by setting up high frequency oscillations of considerable power

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and destructive effect, or may establish an arc, and may then be taken as a measure of the actual voltage of fundamental frequency. It is thus seen that transient voltages are of negligible effect in the absence of a spark gap, but with spark gap connected, with or without test piece in parallel, they may give misleading indications of the actual maximum of normal frequency voltage, and consequent stress in the test piece, or cause abnormal stresses by high frequency oscillations.

Growth of Charge.—It has been observed during high-tension tests that the charge seems to increase with time at constant voltage and frequency, and that at irregular intervals a critical point is reached, causing a flash-over and high frequency discharges at the spark gap in parallel or at some weak point in the test piece.

This can occur without causing a dynamic current to follow, and the length of the spark gap is then not a measure of the normal frequency high-tension voltage. If the voltage is raised very rapidly, it may be carried past the point of high frequency discharge, and a genuine arc produced at the spark gap at a normal frequency voltage corresponding to its length, and considerably in excess of that first observed. This high voltage reading is then taken as the correct one.

Resistance in Circuit.—In order to limit the current and oscillations, resistances of about one ohm per volt are specified to be used in series with the spark gap and this may introduce a disturbing element.

VOLTAMETER COIL IN HIGH-TENSION TRANSFORMER.

This method of measuring the applied voltage is recommended by Mr. Hendricks in place of the spark gap method. He says: "This I consider the most nearly perfect method for determining the high tension voltage with convenience and accuracy. All that is required is a coil of few turns inserted symmetrically at the middle of the high-tension winding and connected thereto at the neutral point. A few turns of the regular winding would do, but for mechanical reasons it is better to use a separate coil. Connection of the windings is imperative, as it is not practicable to insulate the voltmeter coil against half

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the high-tension voltage as is necessary if not connected. Taps should be brought out at 25 per cent. and 50 per cent. of voltmeter coil winding to give convenient voltmeter readings at $^1/_4$, $^1/_2$ and full potential. The accuracy of this method is very great. Although the voltmeter coil is connected at the middle of the high-tension winding, it embraces nearly the same flux as the main winding. Therefore, the voltmeter readings are almost independent of the transformer reactance or ordinary variations in load and power factor."

METHODS OF TESTING.

Conditions of Test.—To obtain exact and definite results, all of the conditions of the test must be accurately known. As it is impossible to duplicate actual working conditions, which are necessarily variable and indefinite, it is best to adopt a standard method of test—one that is simple and direct, and which will give comparative results wherever used. The following data should be accurately known and given: previous history of the test piece and a complete description of its physical make-up and condition, its form, size, thickness, surface, and absorption, if any; the form and intensity of the electrostatic field, temperature, time, frequency, and methods of measurement; size and shape of the electrodes used in applying the voltage, and whether tested in air or under oil.

In general, tests of high-tension insulators should be made under conditions approximating as nearly as possible the average conditions of actual practice and also under the two extremes or limiting conditions, particularly of temperature and of humidity or dampness.

Time.—The time element is found to be most important in testing. Not only is time an important factor due to the growth of charge in the circuit, which consideration has already been discussed, but the results will also depend largely upon the time of application of the stress in all materials which show energy loss and consequent heating. This loss is due to dielectric hysteresis where the insulator has zero absorption, or due to both hysteresis and conduction, if it contains traces of water. When testing in air, heating is also due to static discharges over the surface of the insulator.

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The measurement of energy loss or dielectric hysteresis is very difficult, and often impossible, because of its small magnitude and the high voltage and low power factor involved, but even in insulators where there is very small energy loss and therefor little heating from this cause, the time factor is still important, due not only to the growth of charge in the circuit, but also due to "fatigue" or molecular strains in the dielectric, the same as in other materials under other than electrical stresses.

In general, the voltage necessary to puncture will decrease with increase of time of application of the stress, and it hence becomes necessary to determine carefully the time-voltage curve.[2] In preparing such a curve an average of a number of tests should be used for each point on the curve. Puncturing voltage should first be determined by the instantaneous test. A low voltage is first applied, and is then rapidly and steadily raised until puncture occurs. The time consumed should ordinarily be about ten seconds, which rate of increasing the voltage is not so rapid but that the final voltage can be read correctly to about 1 per cent. Having obtained the maximum or puncturing voltage, successive tests are made at decreasing voltages, which may either be percentages of the puncturing voltage or arbitrarily chosen figures, each being maintained constant until puncture occurs, and the required time noted. Points on the curve are taken until a voltage is reached which may be maintained indefinitely without puncture of the insulator. The heating effect may be marked and have an important influence on the results.

Temperature.—Increase in temperature has for a long time been known to decrease materially the dielectric strength of an insulator.

Henderson and Weimer[3] have shown that a high-grade porcelain changed from an insulator at ordinary temperatures to a conductor at a temperature of about 200° to 225° C., conducting the current without puncturing. The decrease in dielectric strength, while considerable and important, was, however, shown to be relatively small up to 100° C., which is the upper limit of temperature encountered in commercial practice.

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[2] Montgomery and Wilcox, Thesis, Ohio State University, 1907.

[3] Trans. A. C. S., Vol. XIII, p. 469.

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Moisture and Absorption.—The presence of small quantities of moisture is a source of wide variation in the insulating strength of any dielectric. If its absorption is not zero the sample should be thoroughly dried before testing; and if in practice it is used where it may absorb moisture even from the air, it should also be tested in a saturated condition.

In porcelain even a low absorption indicates an immature and poorly vitrified body and consequent decrease in insulating strength.

Wet or spray tests are also necessary in commerical testing of porcelain and glass insulators, but are of interest only in so far as proper design is concerned.

Thickness.—We would expect the dielectric strength of insulating materials to vary in direct proportion to the thickness, but it has been shown by tests on many kinds of materials that in general the dielectric strength varies between the square root and the first power of the thickness, that is, between $y = \sqrt{x}$ and $y = x$. Therefore, unless the law of variation is definitely known, the test must be made upon the actual thickness under consideration, and no reliance can be placed in results given per centimeter or per inch, and based on tests of other thicknesses.

Glass and thoroughly vitrified and mechanically perfect porcelain most nearly follow the straight line law.

Composition.—The question of composition in all high-tension insulating materials is a physical, rather than a chemical, one. The material or insulator must first be of high dielectric strength and free from conducting impurities. It must have the requisite mechanical strength for the purpose for which it is intended. Unless used under oil, it must be non-absorbent. It must be of good mechanical structure, free from flaws or laminations. In the case of high-tension line insulators used out of doors, they must be of such a composition that they will not deteriorate under atmospheric conditions and electrical stress, be of sound and certain mechanical strength, and of long life.

In regard to electrical porcelain, I agree with Bleininger and Stull[4] in the statement that "the electrical resistance seems

[4] Trans. A. C. S., Vol. XII, p. 628.

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to depend more upon sound vitrification and good mechanical structure, than upon chemical composition, excepting in so far as the latter governs the vitrifying behavior." I think also that the work of Watts, who deserves great credit as the pioneer in research work on the effect of composition in electrical porcelain, shows this same statement to be true when viewed in the light of more recent experiments.

Surface.—Mr. Hendricks says that strictly speaking there is no such thing as the "creeping voltage" of an insulator, the voltage required to arc over a clean insulating surface being nearly independent of the kind of material and the character of the surface, but determined by the form and arrangement of the electrodes and the insulation. It depends, he thinks, indirectly upon the capacity of the apparatus considered as a condenser and the character of the dielectric (as air or oil) which is ruptured by the arc, every "creeping" test being also a puncture test, as is obvious.

Contrary to this testimony, I have noted in tests on vitrified clay, porcelain, and glass insulators, providing a variety of surfaces upon which to note the action of the static discharge, that the smoother or more glossy the surface, the longer and more violent would be the brush discharge from a given voltage. In these tests the samples were of the same thickness and, therefore, of the same capacity, considered as a condenser, and the same form and arrangement of electrodes was used in all cases.

Frequency.—Results will vary very slightly with the frequency, as the range of commercial frequencies—25 to 60 cycles—is too small to have any great influence on the results in standard tests. Any variation noted is principally due to variation in energy loss and consequent heating, the higher frequency leading to a lower puncture voltage.

Electrodes.—The electrodes used should be cylindrical with rounded edges to avoid the increase of dielectric flux density due to sharp edges. The diameter of the electrodes is governed by the area of the insulator surface which it is desired to test. The larger the area, the more likelihood of covering existing flaws. Often, when using small electrodes, the puncture will

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occur at some distance from the electrode, thus giving a higher reading than would be given if the electrodes covered the flaw.

Medium of Test.—All tests should be made under conditions resembling as nearly as possible those of actual practice. Tests made in air are not at all comparable with tests made under oil. Insulators and insulating materials, therefore, which are to be used in air, should be tested in air; and those used under oil should be tested under oil. The effects of oil immersion on pieces tested under oil are as follows:

Effect on Test Piece.—When permeable to the oil, the dielectric strength is in general increased by impregnation.

Effect on Electrostatic Field.—The general effect of oil immersion is to eliminate corona and static discharges over the surface of the test pieces, to render the form and intensity of the electrostatic field more definite and uniform, and to concentrate it at the edges of the electrodes.

Effect on Temperature.—This is very marked and consequently of great importance, especially in long-time tests, a large volume of oil tending to diffuse the heat generated and to maintain a constant temperature throughout.

DISCUSSION.

Prof. Stull: From more recent work which has been done on electrical porcelains, I am of the opinion that the composition does influence the dielectric strength. However, it is primarily essential that a porcelain should be well vitrified, but not over-vitrified, in order to give its maximum strength.

In breaking a large number of trials through the line of puncture, we have observed that the passing of the current did not leave a hole, but on the contrary "the hole" was filled with a glassy porcelain which had been fused.

Since there is no substance which is a perfect conductor and no substance which is absolutely a non-conductor, it follows that the conductivity differences of different substances are due to their different resistances. Insulators are merely substances of low conductivity.

When a piece of porcelain is placed between two poles and the voltage gradually increased, the positive pole represents a

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high potential and the negative pole low. A voltage is finally reached that causes some current to flow, which, meeting high resistance, heats up the porcelain. As the temperature of the porcelain increases its conductivity increases, thus allowing more and more of the current to pass. The heat becomes accumulative, causing the porcelain to fuse, and fused porcelain makes a fairly good conductor.

Mr. Minneman: In regard to the cause of the puncture, my experience does not agree with that of Professor Stull, that the puncture is due to fusion of the material.

Prof. Stull: The fused porcelain appears as a thin hair-like line of glass along the line of puncture. The heating of the porcelain is confined to a small area, and the time is very short (almost instantaneous) between the first "leakage" of current when heating begins and final "puncture" when the porcelain has become fused along the thin hair-like line of puncture.

Since the heat is confined to such a small area and the temperature increase so sudden, the heat is soon dissipated by the surrounding oil and the porcelain, hence the temperature of the whole mass of porcelain does not rise perceptibly above the temperature of the oil bath.

It would be a simple matter to determine whether any relation exists or not between the fusion temperature and the dielectric strength of porcelain. If the phenomenon of puncturing is due to force "punching" a hole through the insulator, as electrical engineers maintain, then the dielectric strength of a porcelain would hold a definite relation to its mechanical strength.

A series of experiments touching upon these two points have already been outlined and the work will probably be carried out in the near future.

It would seem that there is some relation between the dielectric strength of a porcelain and its fusion or softening temperature interval, and the softening interval would be influenced by its composition. Porcelains maturing at low temperatures show low dielectric strengths, otherwise why is it necessary for manufacturers of high-tension insulators to employ temperatures of cones 10 to 14?

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NOTE PREPARED AFTER READING THE ABOVE DISCUSSION.

Mr. Montgomery: The consensus of opinion among electrical engineers regarding the mechanical process involved in the rupture of a dielectric under high potential stress is about as follows: There are several phases to the phenomena, and in solids it is probable that several different actions take place. First, there is set up in the dielectric a molecular strain corresponding to the condenser current, then a consequent heating by dielectric hysteresis ensues. This has a very important effect as we know that the dielectric strength of insulators rapidly decreases as the temperature rises, even over a comparatively low range of temperatures. Finally, conduction takes place by means of both conducting impurities and by ionization.

The familiar phenomena of fusion along the path of the current is due to the flow of current after conduction is established, just as any conductor of high resistance will fuse under sufficient current.

Puncture in its most restricted meaning, that is, the actual opening of a hole through the insulator, is due to fusion, but conduction can occur without puncture as is the case in a Nernst lamp glower. Therefore, the fusion point of a given porcelain cannot determine its dielectric strength as a current has already commenced to flow and it has ceased to be an insulator before actual puncture occurs.

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THE EFFECT OF TEMPERATURE ON THE DIELECTRIC STRENGTH OF PORCELAINS.

By GEORGE WEIMER and C. T. DUN, Ohio State University.

INTRODUCTION.

Review of the Published Work of Others.—H. F. Haworth wrote a paper on the "Electrical Qualities of Porcelain with Special Reference to Dielectric Losses" (published in the "Proceedings of the Royal Society of London," Series A, Vol. LXXXI, No. A547). Under the heading "The Conductivity of Porcelain as a Function of the Temperature" (page 231) the following occurs:

Temp. °C.	Specific resistance ohms per cm³.	Temp. °C.	Specific resistance ohms per cm³.
1.63	143.0×10^{12}	40.86	5.7×10^{12}
2.10	141.0×10^{12}	43.03	4.85×10^{12}
16.40	51.5×10^{12}	47.00	4.01×10^{12}
17.00	50.8×10^{12}	50.40	2.64×10^{12}
18.65	42.3×10^{12}	54.01	1.78×10^{12}
20.5	35.5×10^{12}	56.51	1.44×10^{12}
27.32	20.0×10^{12}	58.04	1.11×10^{12}
30.87	14.0×10^{12}	59.12	1.08×10^{12}
34.70	11.8×10^{12}	62.72	0.77×10^{12}
37.03	8.24×10^{12}	64.89	0.64×10^{12}
40.62	6.25×10^{12}	81.93	0.15×10^{12}

The porcelain was tested in an oil bath. And "At each reading the temperature of the porcelain was noted and when the galvanometer swing and temperature had been steady for at least one hour, the average of these readings was taken and the conductivity calculated."

The above table indicates that porcelain may become a conductor if the temperature is carried high enough. However, the specific resistance and the voltage required to puncture porcelain have no direct connection.

A. S. Watts (Transactions of the American Ceramic Society, Vol. IV, page 97) mentions the fact that the dielectric strength of porcelain decreases at higher temperatures. He also gives data from Wideman's "Electricity" (Vol. I, page 560) which shows that the dielectric strength of glass is decreased by increasing the temperature.

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C. Doelter (Chemical Abstracts, **1909,** page 607) found that the resistance of diopside, adularia, quartz, arfvedsonite, mica, hornblende and quartz glass was decreased by an increase of temperature. He regards as the most important result of his investigation the establishment of electrolytic conduction in solid silicates.

The following two groups are found in Doelter's classification of crystals (Chemical Abstracts, **1901,** page 2900).

(*c*) Minerals like chrysoberyl and cassiterite which conduct both electronically and electrolytically at high temperatures; quartz probably belongs to this class.

(*d*) Crystals which are insulators at ordinary temperatures but conduct well electrolytically at higher temperatures, showing noticeable polarization; such are sapphire, silicates and barite.

In an extensive review of literature nothing was found bearing directly on the subject of this research, except that work previously done by Henderson and Weimer.[1]

Object of This Research.—The work done by these last named investigators gave an idea of the scope of work which was to be investigated. This work will cover more especially that region known as the "critical temperature," or that temperature at which porcelain ceases to be an insulator and becomes a conductor, and also to a small extent the effect of composition upon the same.

APPARATUS.

The Transformer.—The transformer used for this test was a high-tension transformer, which has a capacity of 50 kilo-volt-amperes at 250,000 volts and 60 cycles.

The primary coil consists of 63 turns per leg of $^3/_8''$ double cotton covered wire strip. It is separated from the secondary winding by 3.6″ of "Mineral Seal" insulating oil. The secondary coil consists of 21.357 turns on each leg wound in forty coils, of No. 24 B. and S. gage copper wire. The upper coil on each leg has 225 turns, and the one below it has 232 turns sextuple cotton covered, all the other coils having 550 turns each triple cotton cov-

[1] Trans. A. C. S., Vol. XIII. Western Electrician, Dec., 1910. Physical Review, Dec., 1910.

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ered, making a total of 42,714 secondary turns. This gives a ratio of transformation of $42,714/126 = 339$. One half of the entire winding, primary and secondary, is placed upon each leg of a lamented iron core, and the whole is immersed in "Mineral Seal" oil which is contained in a sheet steel tank. The over-all dimensions of the core are 28 inches wide, 43 inches high and 6.2 inches thick. The yoke is 6 inches wide.

To protect the secondary coils from the high frequencies produced by sudden changes in the value of the secondary current, as when the load is suddenly thrown on, the secondary connections terminate in a series of choke coils situated over the center of each leg.

This apparatus gives a frequency of about 1000 cycles per second.

The Regulator.—The impressed voltage on the primary of the transformer was regulated by a transformer regulator consisting of two similar movable coils surrounding stationary laminated iron cores. These coils are attached to a rack and pinion gear so arranged that as one coil is being lowered over one of the iron cores, the other coil is being raised from the other core.

The primary of the high-tension transformer is connected directly across one of the coils of the regulator. Since the E. M. F. is directly proportional to the number of lines of force in the core cut by the coil, the voltage impressed upon the transformer primary is proportional to the same quantity. Hence this E. M. F. can be regulated by raising or lowering the coil of the regulator across which the transformer is connected.

The complete electrical diagram is shown in Fig. 1 and the method of wiring the switchboard in Fig. 2.

The Electro-Static Voltmeter and its Calibration.—The high electromotive forces used in the "break-down" test of insulators are usually measured by means of an electrostatic voltmeter, which is calibrated by the spark gap. The voltmeter consists of two metal plates, one fixed and the other delicately poised. Both plates are thoroughly insulated by oil, and connected to one terminal of the secondary of the transformer. When the transformer is in operation the two plates become charged with like electricity and repel each other. The suspended plate car-

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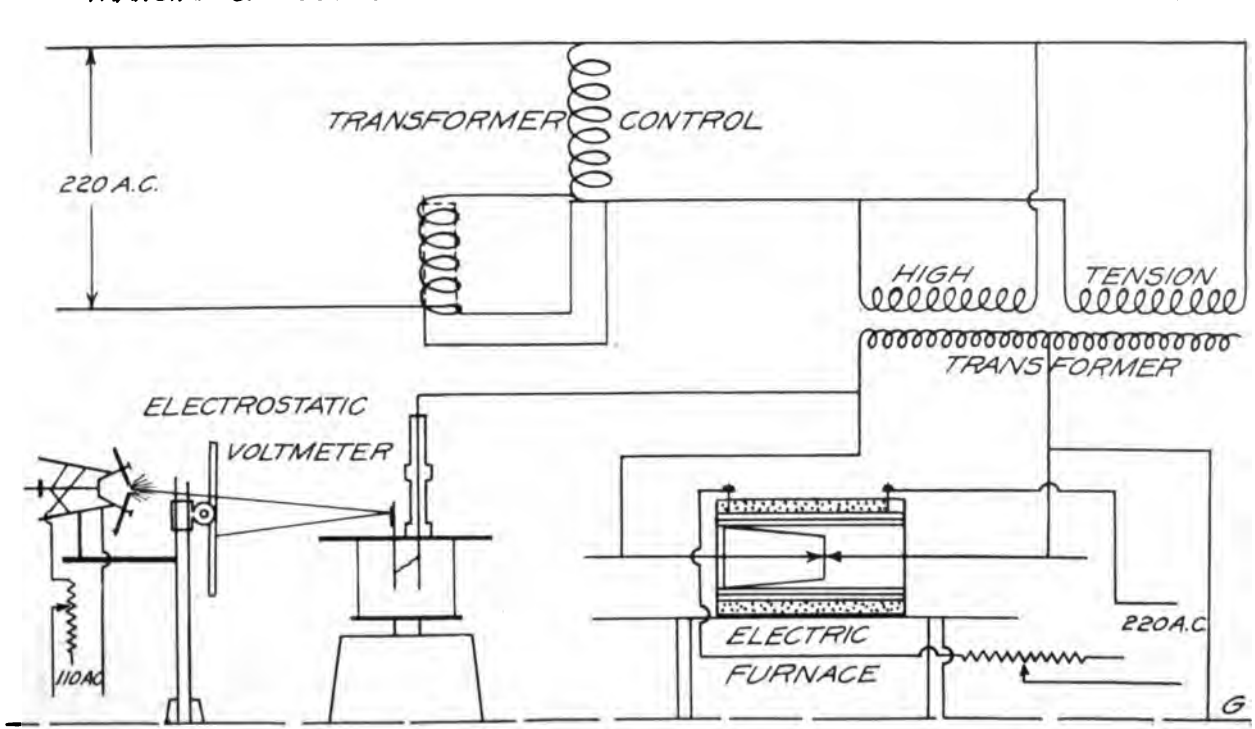

COMPLETE ELECTRICAL DIAGRAM

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TRANS. AM. CER. SOC. VOL. XIV FIG. 2. WEIMER & DUN

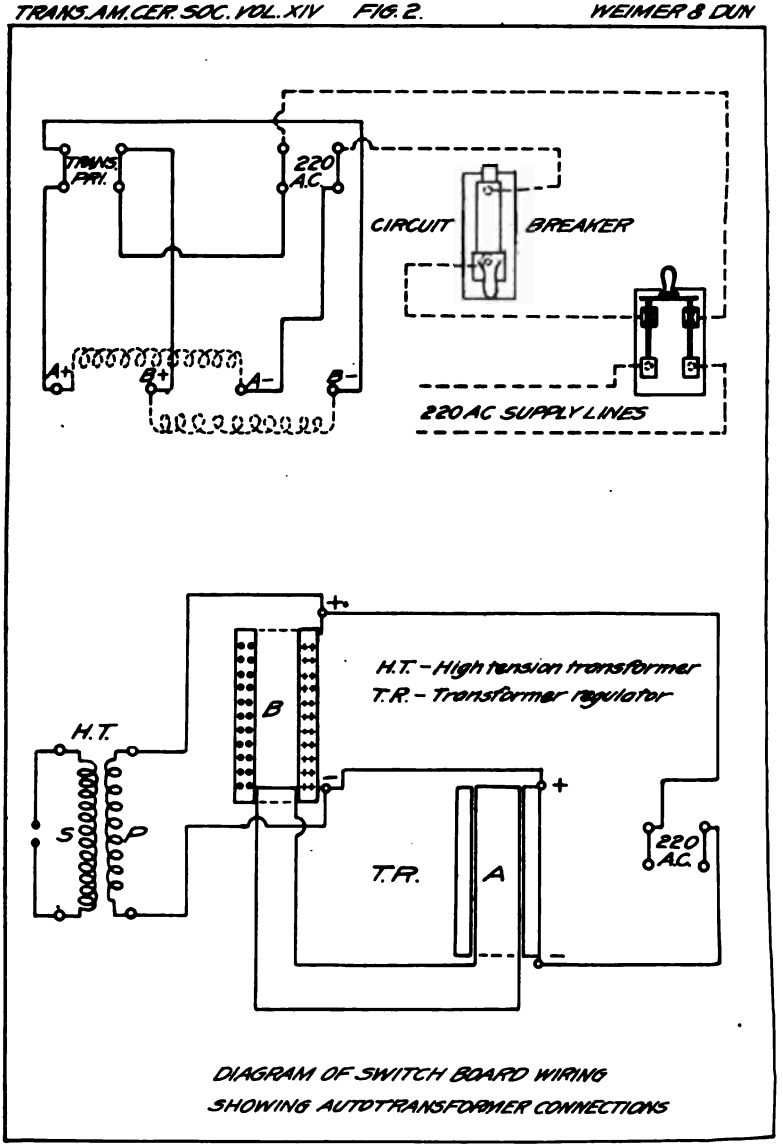

DIAGRAM OF SWITCH BOARD WIRING
SHOWING AUTOTRANSFORMER CONNECTIONS

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ries a mirror which reflects a light onto a scale. On this scale the deflections produced by the repulsion are read and these readings are interpreted as voltages.

The spark gap is set at some definite distance, and then the voltage is regulated until it becomes just sufficient to jump across from needle point to needle point; this produces a certain deflection. For each distance between needle points there is a corresponding voltage, thus the deflections may be interpreted as voltages by means of curves. These readings may be subjected to considerable error on account of the melting of the needle points, drafts of air and the departure of the E. M. F. wave from the sine wave; but by changing the needle points for each reading and by other due precautions, the error may be kept down to less than two per cent. The data for the calibration of the electrostatic voltmeter is given in Table I, and the curves for the same in Figs. 3 and 4.

TABLE I. DATA FOR CALIBRATION OF ELECTRO-STATIC VOLTMETER.

Volts (R. M. S.)	Spark gap (Inches)	Spark gap (Centimeters)	Deflections
5000	0.225	0.57	...
10000	0.47	1.19	0.35
15000	0.725	1.84	0.60
20000	1.00	2.54	0.95
25000	1.3	3.30	1.40
30000	1.625	4.10	1.82
35000	2.0	5.10	2.40
40000	2.45	6.2	3.00
45000	2.95	7.5	3.75
50000	3.55	9.0	4.5
60000	4.65	11.8	6.55
70000	5.85	14.9	9.05
80000	7.1	18.0	11.90
90000	8.35	21.2	14.70
100000	9.6	24.4	17.10

The Electric Furnace.—The electric furnace used consisted of a hollow porcelain cylinder, 9 inches long, $^3/_8$″ thick and 3½″ in diameter, around which was wrapped about 60 turns of No. 19 Nichrome wire. A thick coating of asbestos was plastered over the wires to confine the heat. This furnace is illustrated in Trans. A. C. S., Vol. XIII, p. 471.

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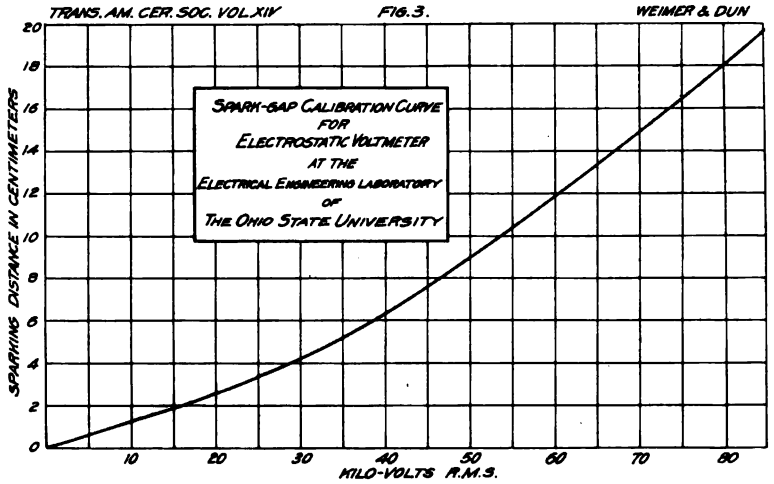

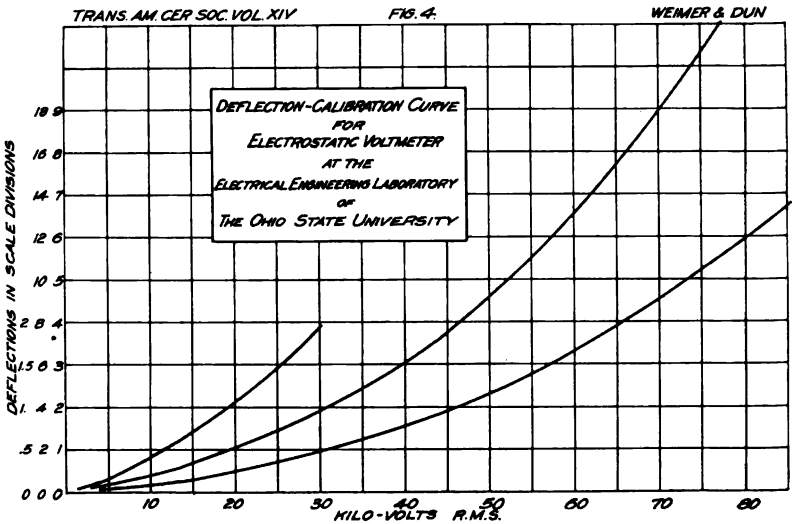

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THE INVESTIGATION.

Composition of Bodies.—There were used in this investigation four different bodies, whose location on a triaxial diagram and compositions are shown on Fig. 5.

In the triaxial diagram the sum of the lengths of the perpendiculars from any point inside the triangle to the base and the two sides is equal to the altitude. Hence for any point the per cent. of one of the ingredients is represented by the length of a perpendicular from the point to the side opposite the apex which represents 100 per cent. of the ingredient.

To secure good working properties for jiggering, the clay content was kept within the limits of 40 per cent. and 60 per cent. 25 per cent. and 35 per cent. feldspar was used in order to have complete vitrification at cones 10 to 12.

Preparation of Samples.—The bodies were weighed up in thirty pound batches. Each batch was placed in a ball mill with about thirty pounds of water and blunged for one hour. The slip was screened through a hundred-mesh sieve and put upon muslin-covered slabs of plaster Paris to dry to a working consistency. Previous to jiggering, each body was wedged by hand upon muslin-covered plaster slabs.

For test pieces cylindrical cups $5^1/_4$ inches high, 0.15 inch thick and 3 inches in diameter were formed by jiggering. The moulds were allowed to stand in the open room until they would deliver; the test pieces were then put in a gas-fired oven to finish drying.

When dry, the test pieces were placed on a cushion of sand in saggars which were then wadded and each one securely covered. The burning was done in a small coke-fired test kiln. Cone 13 on the outside of the saggars was fired down in about 40 hours and inside the saggars cone 11 or 12 was down.

Testing the Pieces.—The test pieces were heated slowly up to the desired temperature in the dielectric furnace in which a mercury-in-glass thermometer was used to determine the temperature. The results are tabulated in Table II. The data in this table are the average of from three to eight trials for each puncturing voltage. The curves in Fig. 6 show the results in graphic form.

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TRANS. AM. CER. SOC. VOL. XIV WEIMER & DUN

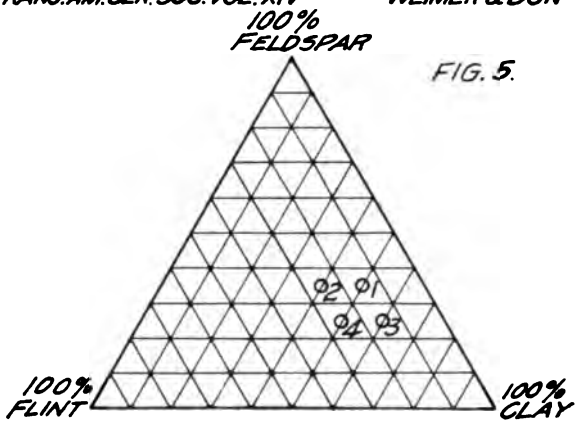

FIG. 5.

COMPOSITION OF BODIES

FIRM HANDLING MATERIAL	No. of Body	1	2	3	4
Johnson & Porter	No.9 Ball Clay	25%	25	25	25
I Mandle Tenn.	Ball Clay No.3	5	5	5	5
I Mandle Georgia	Kaolin	20	10	30	20
Eureka Feldspar Co.	Feldspar	35	35	25	25
Ohio Silica Co.	Flint	15	25	15	25
	Total	100%	100%	100%	100%

ANALYSES

		J&P Ball Clay	Tenn. Ball Clay	Georgia Kaolin	Feldspar	Flint
ULTIMATE	SiO_2	51.2	48.54	45.22	65.87	99.18
	Al_2O_3	32.1	36.25	37.94	19.10	
	Fe_2O_3	.73	.67	.61		.26
	TiO_2	1.4		.96		.01
	CaO	.13	.32	.0	.20	.01
	MgO	0.0	.32	.0		.01
	Na_2O	.1	KHO 0.98	.2	2.56	
	K_2O	.69		.13	12.24	
	Loss on Ignition	13.75	13.94	14.5	.64	.11
	TOTAL	100.10	101.02	99.56	100.61	99.56
RATIONAL	Clay	87.	87.5	94.77	3.08	
	Feldspar	3.	7.39	2.46	95.12	
	Quartz	10.	3.36		2.2	99.18
	Total	100.	98.25	96.23	100.40	

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TABLE II. VOLTS REQUIRED TO PUNCTURE TEST PIECES.

Temp. °C	Body No I	Body No. II	Body No. III	Body No. IV
25	67500	66500	64500	67000
50	67000	66000	64250	66500
75	66000	65000	63500	65500
100	63500	63000	62000	62500
125	59500	60000	59000	57000
150	51500	52500	52500	49500
175	40000	39000	41000	39000
200	27500	25000	29500	26500
225	16000	15000	22000	17000
250	9000	7500	15000	10000
275	5000	4500	11500	7000
300	3000	3500	7000	5000
325	...	...	...	...

At 325° C. for all four bodies the voltmeter showed no deflection for closing the circuit; and when the pieces were retested at room temperature they showed no effect from their former treatment. Furthermore, at 325° C. the electricity appeared to spread and be conducted through the porcelain without forming a white hot arc as it did when the pieces were punctured.

Although the porcelain is a conductor at 325° C., yet it offers a high resistance which requires considerable voltage to push the current through. This accounts for the voltage readings at 325° C. shown on the curves.

Tests were made with a smaller transformer also, which has a capacity of twenty kilo-volt-amperes at 100,000 volts and 60 cycles. For body No. 1 the results are plotted in a dash line in Fig. 6. In every instance for a given temperature the smaller transformer required less voltage to puncture the piece. With the smaller transformer the same results were attained at 275° C. as at 325° C. with the larger transformer. This difference is due to the lower frequency of the smaller transformer. Rayleigh expresses this in the form of an equation, as follows:

$$R_1 = R\left(1 + \frac{P^2 l^2 \mu^2}{12\, R^2} - \frac{P^4 l^4 \mu^4}{184\, R^4}, \text{ etc.}\right).$$

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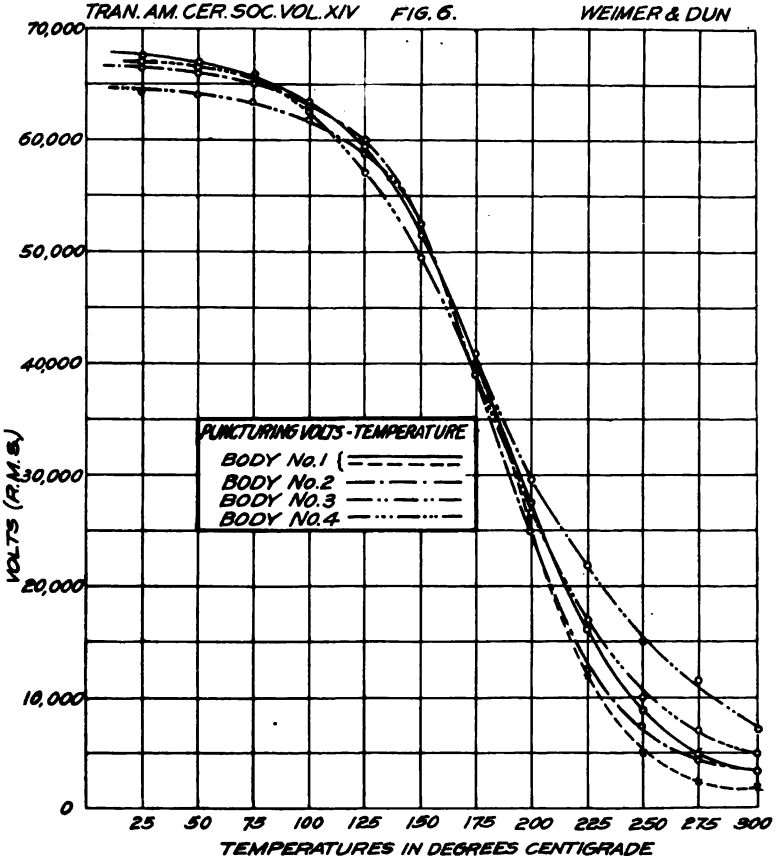
R_1 = new resistance; R = ordinary resistance (by direct current); P = frequency; l = inductance; μ = permeability.

This effect might be explained on two different theories; first (and less probable), that known as "skin effect" due to the high frequency; second, the difference in effect produced by a force directly applied and an alternating force.



Effect of Composition.—Of the ingredients, feldspar seems to have the greatest effect upon the dielectric strength. Bodies No. I and II, highest in feldspar, are weaker at the higher tem-

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peratures than bodies Nos. III and IV, which is no doubt due to the fact that the higher feldspar makes a more glass-like body which becomes softer at a lower temperature than bodies lower in feldspar. Clay added at the expense of flint makes a stronger dielectric at the higher temperatures, as body No. I is stronger dielectrically than body No. II, and body No. III is stronger dielectrically than body No. IV, at the higher temperatures.

CONCLUSION.

Porcelain changes from a dielectric to a conductor progressively with increasing temperature. This transition is gradual, occurs over quite a range in temperature, and is effected by the composition of the porcelain, by the frequency of the current, and by whether the current is alternating or direct.

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THE RELATION BETWEEN THE CRUSHING STRENGTH AND POROSITIES OF CLAY PRODUCTS.[1]

By G. H. BROWN.

The crushing strength of a structural clay product is not of so great importance in itself, since it is seldom subjected to its maximum load in practice. However, crushing strength is frequently called for in specifications and it is usually the aim to secure the strongest material regardless of what the conditions of service may be. The usual practice is to send the material to be tested in whatever shape or form it happens to be manufactured. The degree of burning, the variation in form, and the defects of manufacture are so widely varied that it is exceedingly difficult to compare typical clays as to their development of strength at different stages of vitrification. By manufacturing from typical clays a series of test pieces made on the same machine, burned in the same kiln with the same conditions of burning, it was hoped to get some comparison of typical clays. At the same time the shape of the place best suited for the work could be determined and the methods of testing studied. The investigation is a continuation of part of that described in Volume XII of the Transactions. In the previous work cylindrical test pieces were manufactured from typical clays, and the absorptions and crushing strength developed by different degrees of burning determined. Unfortunately, the results were somewhat erratic, owing to the excessive lamination developed by the auger machine used and to the too great length of the test pieces. Also, the manner of finishing the ends of the pieces for testing was not satisfactory.

By further experimenting it was thought that the influence of these factors could be minimized and more comparable results secured. The procedure was as follows.

PRELIMINARY TESTS.

For the preliminary work a No. 2 fire clay was selected. After grinding and tempering in a Stevenson pan the clay was passed through a small Mueller auger machine and test pieces

[1] By permission of the Director of the Bureau of Standards.

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prepared. Two dies were used, one having an opening 3½" square and the other a circular opening 3½" in diameter. From the square column 3½" cubes and bars 5¼" long were cut; from the circular column, cylinders 5¼" long were manufactured. The bars and cylinders were made 5¼" long so as to have a length equal to 1½ times the diameter. In testing metals and other materials this ratio has been found to give good results. The cubes were prepared with a view to reducing the effect of lamination by decreasing the length of the piece.

BURNING.

Burns were made in a down-draft gas-fired kiln to 900° C., cone 06, cone 3, and cone 10. The duration of burn was about 72 hours in each case. The temperature distribution was good, being within one cone in all parts of the test kiln.

PREPARATION FOR TESTING.

For the testing an Olsen machine of 200,000 pounds capacity, and having one fixed and one spherical bearing plate, was used. In making crushing tests it is essential that flat, smooth surfaces, somewhat parallel to each other and perpendicular to the sides be used. If high points or edges are present false results are obtained. The surface produced by the cutting wire passing through a stiff mud column are too irregular to permit their being used without previous preparation. Usually some material is used to fill up the depressions and give proper surfaces. Materials such as plaster of Paris, neat cement, sheets of lead, or blotting paper are used. If recourse to one of these is not taken the bearing surfaces may be ground so that the material itself is in contact with the head of the machine. If the ends of the test pieces are very irregular, a plaster cap will not entirely eliminate the error due to this cause. The plaster being weaker than the burned clay, the rough edges cut the cap and unequal strains will be developed. The test piece will chip off on the edges and a cracking sound is heard before the ultimate load is reached.

In testing the clay bars, the ends of which are irregular and consequently leveled up with plaster of Paris, the average variation in crushing strength was found to be 10.7 per cent. and the maximum variation as high as 31.0 per cent. While

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considerable of the variation was due to laminated structure, a large part was due to the rough surfaces under the caps.

The edges and corners of the test pieces made up for the preliminary work were slightly higher than the center, giving a slightly concave surface. As a result, the edges spalled off in testing the pieces. In view of this fact, grinding off the edges was resorted to. A surface grinder having a movable table and a revolving emery wheel was used.

The improvement due to the grinding was made evident by testing a set of similar bars and finding that the average variation was only 8.6 per cent. with a maximum variation of 18.6 per cent. It was therefore decided to grind the ends of the test pieces in preference to capping them.

RESULTS OF PRELIMINARY TESTS.

TABLE I.

Test piece	Cone No.	Average length	Average Area sq. in.	Average load Lbs per sq. in.	Average per cent. variation
Cylinders...	900° C.	5.00	10.65	2,511	9.88 surfaced
Bars	900° C.	4.95	11.49	2,774	9.44 surfaced
Cubes	900° C.	3.30	11.40	2,836	9.63 surfaced
Cylinders...	06	4.90	8.55	6,104	11.11 surfaced
Bars.....	06	4.85	10.96	6,052	8.63 surfaced
Cubes.....	06	3.20	10.96	6,087	7.13 surfaced
Cylinders...	cone 3	4.80	8.24	11,756	7.41 surfaced
Bars.....	cone 3	4.75	10.10	14,601	4.95 surfaced
Cubes.....	cone 3	3.15	10.24	14,277	3.24 surfaced
Cylinders...	cone 10	4.80	8.04	6,867	17.15 surfaced
Bars.....	cone 10	4.75	9.86	17,216	13.70 surfaced
Cubes.....	cone 10	3.10	10.18	14,968	7.05 surfaced

900° C. Series.—In this series the average crushing strength in pounds per square inch of the bars, cylinders, and cubes is about the same, the average per cent. variation of the cylinders being 9.88 per cent., of the bars 9.94, and of the cubes 9.63 per cent. The average crushing strength of the cubes is highest, and the average variation in crushing strength of the cubes lowest.

Cone 06 Series.—In this series the average crushing strength is about the same but the average per cent. variation of the cubes

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is lowest, being 7.13 per cent. as against 8.63 per cent. for the bars, and 11.11 per cent. for the cylinders.

Cone 3 Series.—Here the average crushing strength of the bars and cubes is higher than that of the cylinders, the average per cent. variation of the cubes being 3.24 per cent., of the bars 4.95 per cent., and of the cylinders 7.41 per cent.

Cone 10 Series.—The bars have a slightly greater crushing strength than the cubes, while the crushing strength of the cylinders is very low. The average per cent. variation of the cubes is 7.05 per cent., of the bars 6.13 per cent., and of the cylinders 17.15 per cent.

SUMMARY OF RESULTS OF THE PRELIMINARY TESTS.

Behavior in Testing.—The cubes seemed to give the best results throughout. Although the appearance of the fractures was in some cases not equal to that of the bars, the shorter piece seemed to give better results and to decrease the factor of lamination over the other pieces. In three of the four series, the cubes gave a smaller per cent. average variation than the bars and cylinders. With the exception of the cone 10 series, the crushing strength of the cubes was equal to or greater than that of the bars and cylinders. It was, therefore, decided to adopt the cube as a test piece and also to grind the surfaces which were to come in contact with the machine plates.

PART II.

Having selected the cube as the most satisfactory form of test piece, the remainder of the investigation was taken up.

Clays.—In this paper we have limited ourselves to a discussion of six clays, two shales, two fire clays, and two surface clays. The shales Nos. 1 and 2 are used in the manufacture of paving brick; the fire clays Nos. 3 and 4 are of the No. 2 variety and used in the manufacture of building brick. Surface clay No. 5 is of a limy character, and surface clay No. 6 a red burning alluvial clay.

Manufacture.—The cubes were made up in the same manner as those for the preliminary tests. A number sufficient to allow fifteen for each burning temperature was prepared from each

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clay. The cubes were slowly dried in air and then in a steam dryer.

Burning.—Burns were made at intervals of 2 cones, starting at 08 and continuing until each clay had reached its vitrification limit. As before, the burning was in a down-draft test kiln, the duration of the burn being about 72 hours.

Porosities.—The porosities were determined in the usual manner. The pieces were dried and placed in an air-tight tank. After exhausting the air, boiling water was slowly introduced and the tank kept under a vacuum from 3 to 5 hours, the time varying somewhat with the porosity of the pieces. The wet and suspended weights having been determined, the porosities were calculated using the formula $W-D/W-S \times 100 =$ per cent. porosity. The variation in porosities in most of the series was not great. Pieces which showed too great variation were disregarded in computing the averages.

Grinding.—The porosities of the pieces having been determined, the ends were ground off. Most of the grinding was on a lathe grinder having a movable table and a fixed revolving emery wheel. Although the grinding results were satisfactory, it was found that the dust marred the gears and guides of the lathe; and for the latter part of the grinding an ordinary surface grinder, similar to that used on brickyards for grinding arches, etc., was put into service.

On the lathe grinder it was found that with the softer pieces large cuts could be taken with safety, but the vitrified pieces had a tendency to chip and break unless the cuts were small.

Crushing Tests.—All of the pieces were dried before testing. Usually 15 pieces from each series were tested. Pieces which were defective through having been cracked in burning or badly chipped in grinding were discarded. In placing the cube in the machine care was taken to have a good contact. This was accomplished by running the head of the machine down slowly, and at the same time revolving the bearing plate until the load was applied. The machine was operated on slow speed for the first 8,000 or 10,000 pounds and then thrown on full speed. Where the capacity of the 200,000 pound machine was too low, the pieces were tested on the Olsen machine of 600,-

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000 pounds capacity. The behavior of the cubes in testing was good, most of them showing a cone structure the apices of which, however, overlapped owing to the shortness of the piece.

Usually some cracking was heard before the ultimate load was reached, but the point of failure was determined without difficulty. Pieces highly vitrified usually failed explosively, throwing off fragments with considerable force.

Calculations.—From the ultimate load and the area, the ultimate load in pounds per square inch was calculated. The

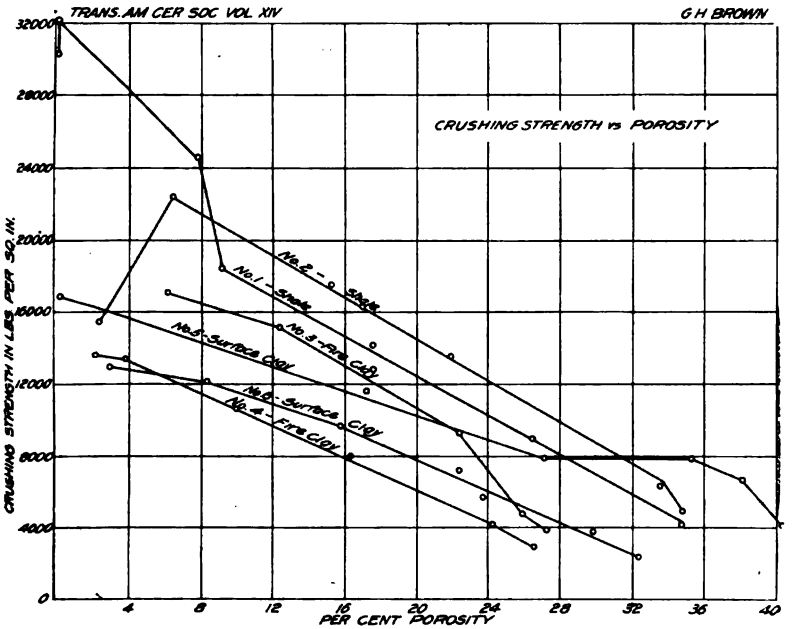

diagram shows the results secured, the average ultimate load in pounds per square inch being plotted against the average porosity.

DISCUSSION OF RESULTS.

The crushing strength of shale No. 1 seems to increase at a uniform rate with a decrease in porosity to 10 per cent. At this point a remarkable increase is shown, the ultimate load increasing from 18,000 pounds per square inch, at a porosity of 10 per cent., to 32,200 pounds per square inch at a porosity of 2.5 per cent.

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From this point the strength takes an abrupt drop, due to the development of a vesicular structure.

The crushing strength porosity line of shale No. 2 is practically parallel to that of shale No. 1, the clay attaining its maximum strength at a porosity of 6.3 per cent. From this point the structure weakens.

The curves of the fire clays are practically parallel to those of the shales at the higher porosities. However, a slight drop is evident in both at the lowest porosity. It was not found practicable to carry both clays to the minimum porosity, owing to the high temperature required. The crushing strengths of both, however, are lower than that of the shales, No. 4 showing the lowest strengths of the series.

Surface clay No. 5, being of the calcareous variety, shows a somewhat erratic behavior. This clay having an initial porosity higher than that of any other tested, the crushing strength increases until a porosity of 27 per cent. is attained. In the manner characteristic of this type of clay, the porosity drops from 27 per cent. to 0 per cent. within a temperature interval of 2 cones. The latter part of the curve is somewhat parallel to that of the others.

The curve of surface clay No. 6, although its general direction is about the same as that of the others, is not so smooth.

SUMMARY OF RESULTS.

Of the six clays shown the shales developed the greatest crushing strength with decrease in porosity. The behavior of the two shales, however, is dissimilar below a porosity of between 8 and 10 per cent. The strength of shale No. 1 increases remarkably, while that of shale No. 2 falls abruptly. This is caused by the difference in behavior of the two shales in vitrification, No.2 having the shorter range. This difference was not observable from the appearance of the piece before testing. The variation illustrates the danger in specifying too low a percentage of absorption or porosity, as both clays do not develop maximum strength at the same low porosities.

The highest individual crushing strength shown was that of one of the cubes made from shale No. 1, burned to practically 0 porosity. With an area of 9.42 square inches, this piece with-

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stood a maximum load of 399,100 pounds or 42,367 pounds per square inch. The crushing strength of this piece was considerably above that of the other members of the series.

CONCLUSIONS.

Bleininger, in Volume XII of the Transactions, shows in one curve the results of tests made on 178 bricks by crushing. The samples were collected from a number of yards and represent both shale and clay brick. The brick were divided into groups according to their absorptions. He states that "On examining this generalized curve it is observed to consist of two parts, *viz.*, approximately a straight line from maximum down to 5 per cent. absorption and a short steep part from 5 to 0 per cent. absorption. It seems quite clear that in the steep portion of the curve the strength increases, due both to the gain in the inherent strength of the solid vitrified clay and to the decrease in pore space." Eliminating the results on calcareous clay No. 5, this statement seems to be borne out by the results shown as far as the lower portion of the curve is concerned. We do not get a steep portion of the curve for all the clays tested. A steep portion was noticed on one of the curves only.

The shape of test piece was a marked improvement over the cylinders used when the investigation was first attempted. Although laminations were still present in the pieces, their effect was greatly reduced by the use of shorter columns.

DISCUSSION.

NOTE PREPARED AFTER READING THE PAPER.

Mr. Kerr: I wish to express my keen appreciation of the work which Mr. Brown has done. It is certainly work of great value to ceramic chemists and work in a field which has been much neglected. The popular assumption that maximum strength always accompanied minimum porosity has, no doubt, been responsible for the failure of many wares which, if properly handled, would have been satisfactory.

I am pleased to note the comparison Mr. Brown has made of the results obtained by using test pieces of various shapes. I have never carried out so elaborate a comparison, but from less complete data I have reached the same conclusion that the cubical

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test piece with ground surfaces is the most suitable and most reliable for ordinary use.

It seems almost impossible to get a capping material which will give constant results in tests made upon samples of the same material. The only practical method in my estimation is to grind plain surfaces as Mr. Brown recommends.

In studying mixtures of feldspar, clay and flint, especially within the range of rather low porosities, it has been my experience that the maximum crushing strength seldom occurs at minimum porosity. As a rule the maximum crushing strength occurs quite a little before minimum porosity is reached; and, so far as I know, there is no way of telling what porosity will be found at maximum crushing strength except by making the tests. It seems that mixtures which show porosity-temperature curves of fair regularity (that is, free from sudden and erratic changes) are more apt to have the maximum crushing strength occurring at nearly minimum porosity than are such mixtures as have irregular porosity-temperature curves. Whether or not such generalities would be applicable to the ordinary structural clay products I cannot say, but I would expect them to apply.

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STUDIES OF FLINT CLAYS AND THEIR ASSOCIATES.

By SYDNEY L. GALPIN, Ithaca, N. Y.

INTRODUCTION.

Non-plastic fire clays have been recognized for many years as a type differing distinctly from the plastic fire clays, yet the investigation of their nature and origin has received but little attention. Their geologic occurrence and distribution in Maryland,[1] Pennsylvania,[2] Ohio,[3] Kentucky,[4] West Virginia,[5] Missouri[6] and Washington[7] have been briefly described by different authors; and they are also known to occur west of Pueblo in Colorado.[8]

Greaves-Walker[9] discusses the sedimentation of the Kentucky flint clays and concludes that they were deposited in basins of rather limited area. Hopkins[10] has argued from a study of some of the Pennsylvania fire clays that they were once the soil in which the flora of the coal beds flourished and that they owe their purity largely to the leaching action of the plant roots.[11] He also points out an explanation of flinty nature similar to Wheeler.

Wheeler[12] has described in detail the flint clays of Missouri. He considers them to be sediments deposited in limestone sinks and purified by the leaching of carbonated meteoric waters. Their non-plastic quality may be due to crystallization of kaolin-

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[1] Md. Geol. Surv., Report on Allegheny County; Ries, Clays of Maryland, Md. Geol. Surv., Vol. IV, Pt. III.

[2] Hopkins, Clays of Western Pennsylvania, Ann. Rept. Penn. State College, 1897; Woolsey, Clays of Ohio Valley in Pennsylvania, Bull. 225, U. S. Geol. Surv.; Lines, Clays, and Shales of Clarion Quadrangle, Bull. 315, U. S. Geol. Surv.; Shaw and Munn, Foxburg Quadrangle, Bull. 454, U. S. Geol. Surv.

[3] Newberry, Geology of Ohio, Vol. III; E. Orton, Jr., Geol. Surv. of Ohio, Vol. VII, Part 1.

[4] Greaves-Walker, Flint Fireclay Deposits of N. E. Ky., Trans. A. C. S., IX, 1907; W. C. Phalen, Clay Resources of N. E. Ky., Bull. 285, U. S. Geol. Surv.

[5] Grimsley and Grant, W. Va. Geol. Surv., Vol. III, 1905.

[6] Wheeler, Clays of Missouri, Vol. XI, Mo. Geol. Surv.

[7] Shedd, Clays and Clay Industry of Washington, June, 1910.

[8] Personal communication, H. Ries.

[9] Loc. cit.

[10] Loc. cit.

[11] If this theory is correct it seems curious that many clays underlying coals are so impure.

[12] Loc. cit.

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ite, because of their coarsely platy structure as seen under the microscope.

Others have made preliminary microscopic examinations which will be discussed later.

The investigations, upon which this paper is based, were undertaken with a view to determine if possible the nature of the differences between plastic and non-plastic fire clays. They were carried on partly in the field and in part at the geological laboratories of Cornell University.[13] The field work included a study of the refractory clays at the following localities: Strasburg, Ohio; Clarion, Pa.; Woodland, Clearfield County, Pa.; Mt. Savage, Md.; and Olive Hill, Ky. Many sections from these localities were also studied under the microscope.

DETAILED ACCOUNT OF OCCURRENCES.

In presenting the results of this investigation it seems best to give the details of the occurrence, petrography and other properties first; and then to explain the views or theories formulated as a result of these studies.

STRASBURG, OHIO.

The plastic and non-plastic clays of Tuscarawas County are found at several horizons in the Lower Productive Measures (Alleghany series). Probably the most important flint clay is that worked about two miles east from Strasburg by the National Fire Brick Company. The bed outcrops only near the crests of the higher hills and seems to be at the same horizon as Newberry's[14] No. 7 coal, which is thought to be the equivalent of the upper Freeport coal.

An unusually good exposure exists in the company's open-cut workings from which the accompanying sketch shown in Fig. 1 is taken. The clay bed consists of three divisions, *viz.*, a lower, No 1 grade fire clay; a middle, flint fire clay; and an upper, No. 2 grade fire clay.

[13] The author is pleased to acknowledge his indebtedness to Professors Ries and Gill for counsel and assistance in conducting the work, and to the National Fire Brick Co., The Harbison-Walker Refractories Co., The Union Refractories Co., The Olive Hill Fire Brick Co., and Mr. Wm. Ramsay, of Mt. Savage, Md., for courtesies and aid in obtaining materials.

[14] Geology of Ohio, Vol. III, p. 66.

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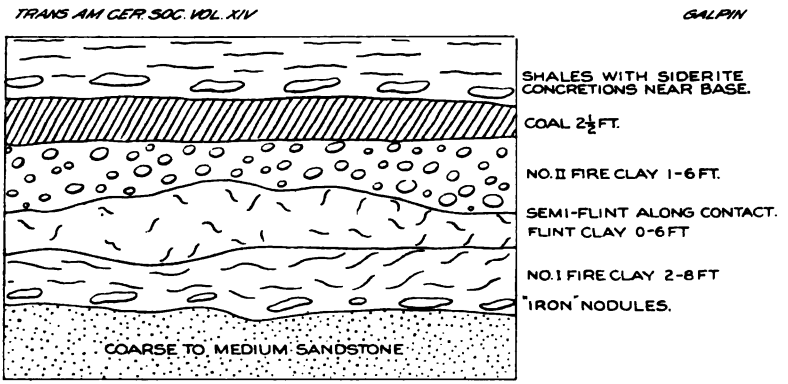

Fig. 1.—Section at Strasburg, Ohio.

The No. 1 fire clay is a gray laminated rock having an irregular hackly fracture. It shows some variation in color and texture, becoming more sandy toward the bottom, where occasional clay-iron stones may be seen. It is frequently contorted and always cut by a network of slickensided slip planes. Though hard when mined it becomes somewhat plastic when ground in a wet-pan. Its thickness is rather variable, due to "rolling up" in places and "squeezing out" in others. The clay rests upon an even sandstone floor but its upper boundary, though usually well defined, is irregular.

The flint fire clay has a massive appearance and is broken up into blocks by irregular joints, but slip planes so characteristic of the surrounding clays are wanting. It breaks with a clean conchoidal fracture, showing a light buff surface mottled by greenish gray lenticular markings, and lined in an irregularly concentric manner by bluish bands or ribbons. The latter seem to be generally grouped about bunches of small pyritic concretions. Upon exposure the clay breaks up into angular fragments stained by the decomposition of the pyrite. Carbonaceous material is locally present in quantities sufficient to produce a black clay. The thickness of the flint clay is decidedly variable, there being frequent marked swells and pinches. The boundary between the flint clay and the No. 2 fire clay is indefinite, the term "semi flint" describing the transition clay, as it is made

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up of lenses of flinty clay more or less surrounded by the slickensided and more plastic variety.

The No. 2 fire clay bears a close resemblance to the No. 1, but shows perhaps even greater contortion and variation in thickness. Its upper contact with the base of a three foot coal bed is even and regular.

The total thickness of the clay bed is fairly constant, variations of one kind being compensated by reciprocal changes in thickness of the others. The strata of the region show no signs of regional disturbance, indicating that the movements in the clay bed were of local nature.

MICROSCOPIC PETROGRAPHY OF THE STRASBURG CLAYS.

Section I.[15]—This represents the flint clay of this locality. With low magnification (40–80 dia.) one sees a fine more or less angular ground mass traversed by irregular veins usually under 15 microns in width, which are bordered by a brownish scum of limonite (?) and filled with material similar to the general ground mass. Numerous small pyrite crystals lie in this scum (see Plate I, Fig. 1) and a few are scattered through the clay. Spherical, radiated concretions of pyrite or marcasite (0.5–1 mm. dia.) are occasionally found.

Greater magnification (400–600 dia.) shows scattered angular quartz grains, a few scales of muscovite and rarely rounded zircons. None of the above exceed 10–15 microns in length. The bulk of the clay is made up of plates or grains less than 2 microns diameter, many of which show low interference colors in polarized light. From their similarity to determinable plates in other sections, they seem to be kaolinite. Sixty per cent. of the clay is estimated to be visibly crystalline, the balance being, in all probability, mainly colloidal in nature.

Section II.—This shows the contact of flint clay with the underlying semi-plastic fire clay.

The part of this section representing the "semi-plastic" clay is more coarsely and thoroughly crystalline than is that of the flint clay (Plate I, Fig. 2). Some areas of the "semi-

[15] Except where especially noted, these descriptions are of thin sections cut from the solid clay, and not of mounted powders.

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PLATE I.

Fig. 1.—Section of flint clay, Strasburg, O., between crossed nicols. Dark spots are pyrite. Large light grains quartz, small ones partly kaolinite × 60.

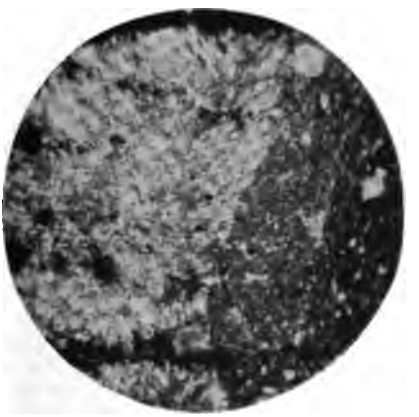

Fig. 2.—Section from Strasburg, O. Shows line of contact, the darker portion representing flint clay and the lighter portion the semi-flint clay with high development of the hydro-micas × 160.

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plastic" are seen to be more highly crystalline than others, indicating varying stages of recrystallization. The platy grains are so interlocked and intergrown that there seems to be no doubt of their recrystallized nature. Most of these plates and aggregates resemble muscovite closely, except that they do not show as strong double refraction as that mineral. It was noted, however, that this property varies in different individuals, and that in a single section crystals may be seen which would form an unbroken series whose birefringence varies from that of muscovite to nearly or quite that of kaolinite. To distinguish these plates from muscovite and kaolinite, they will be mentioned as *hydro-micas* and discussed more thoroughly in a later paragraph.

Scattered through the felt of hydro-micas are occasionally columnar or fan-shaped aggregates of plates, showing low interference colors, low index[16] and the direction of greatest elasticity cutting across the plates. The optical character could not be determined in any of the plates in this section, but a similar plate in Section 14 gave a negative biaxial figure. These properties agree with those given by Iddings and Johannsen for kaolinite.

Hickling[17] has found the index of kaolinite in some of the English china clays to be nearer 1.56 than 1.54. Furthermore, A. B. Dick[18] describes one kaolinite which is optically positive rather than negative and whose mean index is about 1.563, while another he finds is negative. From this he concludes that there are two varieties of kaolinite. Among others who have described various forms of kaolinite crystals are Johnson and Blake,[19] who first used the term kaolinite, Merrill,[20] Reusch,[21]

[16] The index of similar plates in the powder of clay No. 1 was fixed at about 1.54 by the use of "index liquids." The strength of birefringence was determined by measuring the thickness of grains cut normal to the basal cleavage, by focusing on first the top and then the bottom of the grain, reading the difference on the micrometer head and correcting for index to give the true thickness. Knowing the thickness of a grain and its interference colors, the birefringence may be determined with fair accuracy.

[17] China Clay, Its Nature and Origin.

[18] Supplementary Notes on the Mineral Kaolinite, Mineralogical Magazine, XV, p. 124–7.

[19] Am. Jour. Sci., ii, XLII.

[20] Non-metallic Minerals.

[21] Neues Jahrb. fur Min., 1887, II, p. 70.

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Rieke,[22] Cook,[23] Mellor[24] and Ries.[25] All of these investigators have recognized the peculiar sheaf and fan-shaped bundles of more or less hexagonal plates. It seems that there are then kaolinites of different optical properties, which may well represent simply different members of an isomorphous series, containing, perhaps, small amounts of alkalies or other elements in place of hydrogen in the theoretical molecule.

The prisms and fans of this section frequently show "ribs" or plates of higher index and birefringence intergrown with those of kaolinite (Fig. 2). These "ribs" show practically every grade of variation between kaolinite and muscovite.

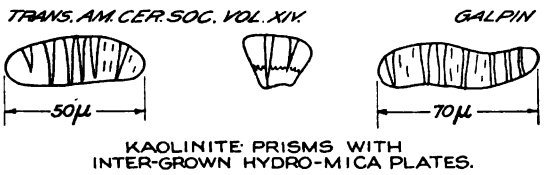

Fig. 2.—Sketch.

Irregular and often corroded quartz grains (under 80 microns dia.) make up about 15 per cent. of the crystalline material of the section. Zircon grains are frequently to be seen. Rather angular cloudy patches (under 100 microns dia.) are sometimes found and may represent the remains of decomposed feldspar fragments. Microscopic crystals (octahedral) of pyrite are abundant near the contact, where they were formed, probably as the result of the reduction of iron sulphate in solution by organic matter from the clay.

Section IV.—This was prepared from the powder of the upper fire clay (plastic); sixty to seventy per cent. of it seems to be in the form of small plates or scales, some of which are muscovite, but more show the lower interference colors of the hydromicas. No grains were seen which could be determined with certainty as kaolinite. Small quartz and zircon grains are present in slight quantities. The texture and mineral content of

[22] Sprechsaal, XL, 1907.
[23] Clay Deposits in New Jersey, N. J. Geol. Surv., 1878, pp. 280–281.
[24] Trans. Eng. Ceram. Soc., Vol. VIII, 1908–9.
[25] Md. Geol. Surv., IV, Pt. III.

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the powder is similar to those of the powdered plastic clay from Mt. Savage (compare Section XIX).

Section VI.—Prepared from the powder of the "semi-flint" clay found between the upper plastic and flint clays.

The powder resembles that of the plastic clay except that some of the grains are not composed of a single flake or plate, but are made up of a large number of small plates still tightly bound together. (Compare with powders of Olive Hill semi-flint and Mt. Savage plastic clays.) Individual grains do not exceed 30 microns diameter. When lying flat in the section, their birefringence is very low and they may be distinguished from kaolinite only by their higher index of refraction. When on edge, the higher interference colors mark most of them as hydro-micas and muscovite. Only a few plates of kaolinite were seen. These show an index of refraction of about 1.54, and become dark in polarized light. A few quartz and zircon grains were also noted.

RESULTS OF DEHYDRATION TESTS.

The microscopic examination of these clays led to the belief that there should be decided differences in the water content of the flint, semi-flint and plastic clays. In order to test this view a 15 to 20-gram sample of each type was powdered, dried at 112° C. and then ignited to approximately constant weight, with the following results:

	Per cent. drying loss	Per cent. ignition loss	Per cent. total loss
Flint clay	0.8	12.3	13.1
Semi-flint clay	0.56	8.05	8.61
	0.5	7.87	8.37
Plastic clay	0.1[26]	7.33	7.43

For purposes of comparison a direct determination of the water in the plastic clay was made according to the Penfield method, giving: H_2O = 6.9%, other volatile matter (CO_2, SO_2, etc.) = 1.0 per cent., total loss = 7.9 per cent. This clay was taken for the Penfield determination because it contained con-

[26] Had been previously dried on a radiator.

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siderable visible pyrite, and was expected for that reason to show a higher percentage of volatile matter, exclusive of water, than the other clays. It seems safe to conclude that with most of the clays tested, more than 90 per cent. of the ignition loss may be safely considered to be water.

The results were significant, in that they show the impossibility of much kaolinite in either the semi-flint or plastic clays. Commonly the low water content of a clay may be attributed to the presence of excessive amounts of anhydrous minerals, but microscopic evidence is against such an explanation in this case. Since the samples tested represent clays ranging from the middle toward the upper boundary of the bed, the results seem to throw some light on the geologic history of the clays, which consideration will be taken up later.

CLARION COUNTY, PENNSYLVANIA.

In this county, as in the region around Strasburg, Ohio, valuable fire clays exist at several horizons ranging from the Mercer to the top of the Alleghany series.[27] The clays investigated were collected at mines located from five to seven miles northwest of Clarion. Some specimens were taken from stock piles and others secured in the mine tunnels. The geologic relations at one of the mines is shown in the sketch (Fig. 3).

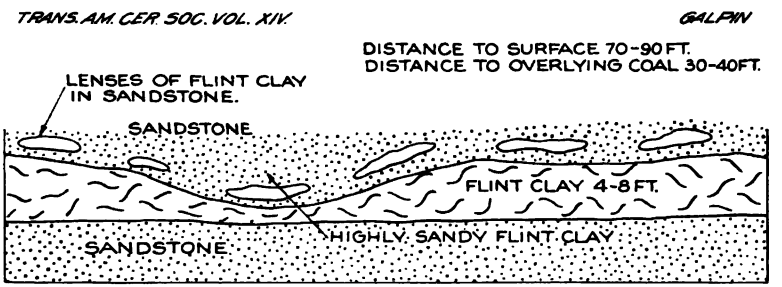

Fig. 3.—Section at Clarion, Pa.

The clay lying between massive sandstone beds is all non-plastic, and occurs in somewhat lenticular masses, which at times grade into sandstone if followed along the bed. The

[27] Bull. 315, U. S. Geol. Surv.; Bull. 454, U. S. Geol. Surv.

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thickness varies from 0 to, perhaps, 16 feet. Variations of color and texture may be noted, mainly in crossing the bed vertically, but also in following it horizontally. The better grades of clay, usually found toward the middle of the bed, are of a cream or buff-gray color, and show a clean, smooth conchoidal fracture. All gradations from this type into a clayey sandstone of dull gray color and rough fracture may be found.

Although no coal lies directly above this clay, it seems probable that the horizon is that of the Lower Kittanning coal, which is sometimes missing in this locality.[28]

The strata of the region show only slight evidence of dynamic disturbance.

MICROSCOPIC PETROGRAPHY OF CLAYS FROM CLARION CO., PA.

Section VII.—This section is from a very smooth buff variety of the Clarion clay which shows a tendency to split into flat slabs. The type occurred as a layer 12 to 18 inches thick, but is now worked out.

Under the microscope, the clay is seen, in the main, to be finely crystalline, although the section is somewhat clouded by a limonite scum. In places, recrystallization of knots or bunches of kaolinite prisms has pushed the scum out into rims, which may be noted without magnification as brownish spots or circles upon the surface of the clay. Other than these recrystallization structures, the section presents a rather even and homogeneous appearance.

Kaolinite, in prisms under 50 microns length, fans, and vermicular forms, composes from 65 to 70 per cent. of the clay. "Ribs "of the hydro-micas are seen in only a few of the prisms and fans.

Rhombohedrons of siderite ($FeCO_3$) often 60 to 70 microns in length are evenly scattered through the section. They seem to have been among the first crystals to form after the sediments were laid down. Other less common minerals are quartz in badly corroded grains up to 90 microns length, zircon grains, rutile in needles, tourmaline grains, and a few small recrystallized plates of muscovite.

[28] Bull. 315, U. S. Geol Surv.

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Section VIII.—This is slightly sandy flinty clay, and the section is similar to VII in general, but shows no siderite and contains more and larger detrital grains of quartz, zircon and tourmaline. Mica plates are slightly more abundant, many of them seeming to be recrystallization products.

Section IX.—This represents a variation which is so sandy that it is discarded at the mines. It comes from near the top of the bed (Plate II, Fig. 1). Quartz grains with very irregular outlines make up about 50 per cent. of the rock. The groundmass is similar to that of Sections VII and VIII, but shows little or no muscovite. The development of hydro-mica is more marked than in any of the foregoing clays from Clarion.

Section X.—A darker somewhat sandy phase of the Clarion clay, which is mottled with occasional black, waxy patches or lenses.

In general, this section resembles Nos. VII, VIII and IX, but has few of the spherical recrystallization forms. There is a larger amount of the brown or gray "scum" which may here be in the nature of organic matter. A section was cut across one of the black waxy lenses which under the microscope was seen to be clearer, extremely fine, crystalline material. The minerals could not be identified. It seems that contraction of the clay had opened slight fissures which were filled by this fine-grained material, probably from other parts of the same bed.

Section XI.—Typical flint clay, Clarion, Pa. This clay differs from No. VII mainly in showing no tendency to break or cleave in any one direction more than in any other. It is buff in color and has a medium conchoidal fracture.

Under the microscope, its structure resembles that of No. VII, but there are more of the recrystallization features, two generations being visible. (Compare with Sections XX and XXI.)

Kaolinite occurs abundantly, (1) filling the clear spaces in the recrystallization spots, (2) in prisms, and (3) in irregular felts throughout the section.

The prisms are frequently ribbed with hydro-micas. One or two instances were noted where a mineral grain determined

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PLATE II.

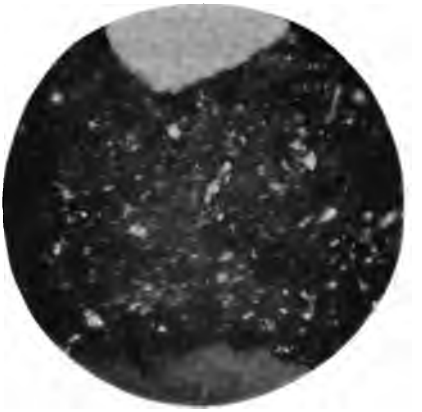

Fig. 1.—Section of sandy flint clay from Clarion county, Pa., between crossed nicols. Shows edges of two corroded quartz grains. The long grain seen near the center of the section is a kaolinite prism. A few mica flakes may be seen as needle-like grains × 200.

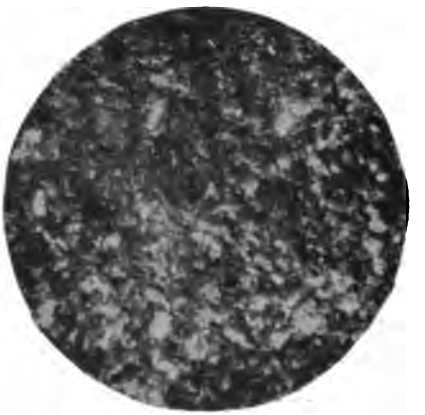

Fig. 2.—Soft clay, Woodland, Pa., between crossed nicols. Shows coarse mat of plates with scattered muscovite grains or flakes × 60.

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as epidote, representing probably the recrystallization of traces of calcium with the silica and alumina, lay toward the center of one of these prisms and on either side of it, the ribs being developed to an especially strong degree. Some kaolinite fans were noted which were ribbed with plates showing the birefringence of muscovite. In all cases these plates are clear cut, sometimes extending beyond the kaolinite, and showing no evidence of decomposition into kaolinite. The evidence seems more to favor the view that the hydro-micas have developed with the kaolinite.

DEHYDRATION TESTS OF CLARION, PA., CLAYS.

Inasmuch as the various phases of the Clarion flint clay do not show much mineralogic difference, it was not expected that there would be so marked variation in their water content. Only two samples were dehydrated, one being the smooth buff clay described under Section VII and the other the sandy phase (Section IX). The results of these tests are given in the following table:

	Per cent. loss 112°	Per cent. loss ignition	Total
7 Flint clay	0.55	13.45	14.0
9 Sandy flint	0.03	12.17	12.20

The variation found is due mainly to the greater per cent. of quartz in the sandy clay. Carbon dioxide is responsible for some of the percentage loss in No. VII as it contains numerous grains of iron carbonate.

WOODLAND, CLEARFIELD COUNTY, PENNSYLVANIA.

The clay underlying the Mercer coal is economically the most important in this locality[29] although other horizons produce considerable amounts of refractory material.

Near Woodland this bed outcrops near the base of the hills and not many feet above stream level. It lies in a nearly horizontal position, but has been affected somewhat by the folding and faulting without changing the nature of the clay to any extent. The No. 1 mine of the Harbison-Walker Company

[29] Bull. 285, U. S. Geol. Surv., Clays and Shales of Central Pennsylvania.

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is crossed by one fault whose throw varies from 8 to 40 feet. It extends in a northwest direction or normal to the axis of general folding in the region, and is said to continue at least two miles to the southeast where it is encountered in another mine.

An ideal section given in Fig. 4 may serve to show the occurrence.

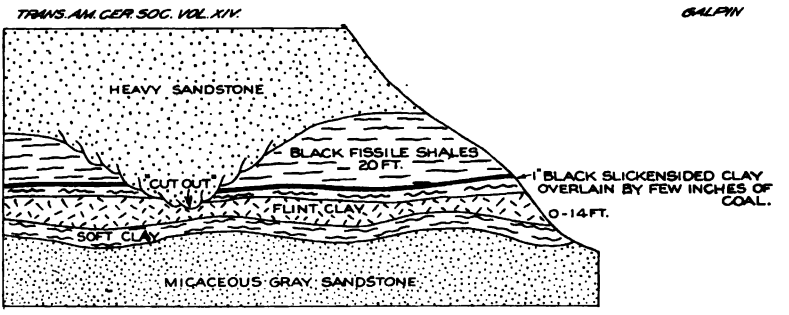

Fig. 4.—Ideal section at Woodland, Pa.

(1) The "soft" clay is a gray laminated rock with rough fracture and cut by numerous interwoven slip planes. It is fairly smooth but contains many flakes of mica which are quick to catch the eye. Though not truly plastic it is said to be a good bond clay. Its boundary with the flint clay is irregular and often difficultly determinable.

(2) The flint clay is also gray, often mottled with dark, irregular blotches, giving it the appearance of a breccia. The fracture is roughly conchoidal, and the mass is broken by irregular seams or joints whose sides are usually coated with limonite and sometimes clear tabular crystals of barite. The occurrence of barite with fire clays is somewhat unusual, but was noted also at Olive Hill, Ky. The crystals were probably deposited by the reaction of pyrite on solutions of barium hydrate or carbonate. The bed is variable in thickness, and to some extent in quality. One instance was noted where the clay is completely cut out by the overlying sandstone which appears to have settled and squeezed the clay out as its surface was crossed by a series of rough steps (Fig. 4).

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Above the flint clay there is usually a thin layer of smooth black clay, with a few inches of coal at the top and over this some 20 feet of material called "Black Shelly." This is a dark shale which breaks up into thin planes on exposure to the atmosphere. The sandstone is normally found above this shale.

In one instance, a more plastic clay is found above the flint clay and it is interesting to note that water is reported more abundant in its vicinity.

MICROSCOPIC PETROGRAPHY OF THE WOODLAND CLAYS.

Section XIV.—"Soft clay," Woodland, Pa. This specimen is one of the most interesting of those examined microscopically.

With low powers (magnification 40 to 80 diameters) it is seen to be highly crystalline, and made up of a felt of mineral plates, which show a variation of from 5 to 200 microns in length or diameter. The clay is not microscopically homogeneous, that is, there are areas or patches which seem clearer than others (compare Section XV), and these often show slightly lower interference colors, although the felty structure is similar to other parts (Plate II, Fig. 2).

There are three prominent types of mineral grains: (1) Large plates 100–250 microns (though sometimes smaller) showing when on edge parallel extinction, and high interference colors. These plates are fairly evenly distributed through the section. Several determinations show that they are muscovite and may represent detrital material, although there is nothing other than their size to indicate this. Frequently these plates are bordered by an irregular growth of parallel orientation which shows lower index of refraction and lower order interference colors. These rims do not seem to be the result of weathering because of their irregular shape and also because the boundary between them and the muscovite scales is clean and well marked. The muscovite shows good cleavage cracks while few or none are to be detected in the bordering mineral. They, therefore, seem to be additional growth of hydro-mica upon the muscovite and indicate simply that crystallization of the border took place after the available alkalies for the formation of muscovite had been exhausted (Fig. 5).

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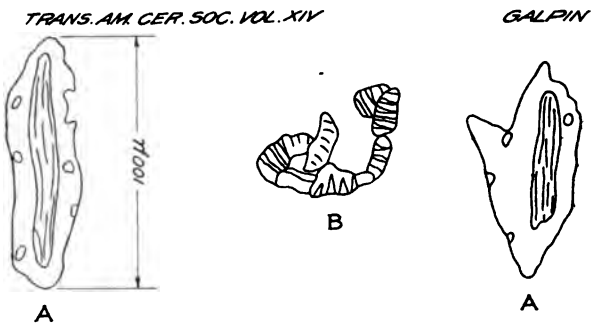

Fig. 5.—Sketches.

While conspicuous, these plates make up a small per cent. of the clay.

(2) Plates which are in general similar to (1) but smaller and of lower index and birefringence make up the bulk of the section. They usually lie in a confused felt-like mass, but sometimes show parallel orientation over considerable areas. (Compare Section XVII.) Occasionally they form fan-like aggregates closely resembling kaolinite but having usually higher index and birefringence. These are believed to be hydro-micas.

(3) Kaolinite in prisms, fans and plates is present. The commoner shapes are represented in accompanying sketches (Fig. 5, B).

"Ribbing" is always present to a considerable extent in these kaolinite prisms (Plate III, Fig. 1). Where any orientation could be detected the long direction of the prisms lay parallel to the direction of elongation of the mica plates, which would make the cleavage of one perpendicular to that of the other. The tendency sometimes noted, for crystal plates and prisms to lie with their long directions roughly parallel, probably represents movement within the clay under pressure.

Occasional groups or bunches of kaolinite prisms irregularly set together may represent the weathering of feldspar fragments, although it seems more probable that they are remnants of the

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PLATE III.

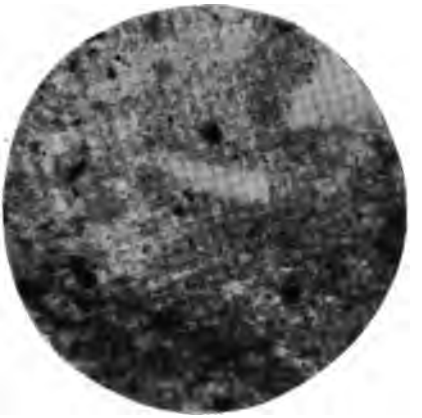

Fig. 1.—Soft clay, Woodland, Pa., by direct light. Kaolinite prisms showing ribs of higher index of refraction × 300.

Fig. 2.—Flint clay, Woodland, Pa., between crossed nicols. Shows only the larger crystal grains which are mainly kaolinite, often "ribbed." A few bunches of the hydro-micas may be noted × 200.

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knots or concretions of kaolinite so commonly seen in the more flinty clays.

Quartz and zircon in small grains are present but inconspicuous and probably rare.

Rounded tourmalines were noted but are unimportant. Rutile (?) needles of small size seem fairly abundant, sometimes so grouped that they suggest recrystallization products from the weathering of some mineral such as biotite. On the whole, there is, however, no definite evidence of detrital material other than quartz and zircon in this clay.

Section XV.—Mottled, or "conglomerate" flint clay, Woodland, Pa.

This section is composed largely of visibly crystalline material, although the largest individuals rarely exceed 20 microns in greatest dimension. The average size of grain is 5 to 10 microns although there is much finer material (Plate III, Fig. 2). The structure throughout is fairly uniform, but one notices that there are areas clearer than others which with slight magnification resemble sharp, irregular fragments embedded in a more turbid ground mass. With higher magnification, it may be seen that one part is much clearer than the other, although both seem equally well crystallized. The clear areas are found by comparison with the rock chip from which the section was cut to represent the dark patches which give the clay its brecciated or "conglomerate" appearance. Mineralogically there are some differences. The clear areas are composed almost entirely of kaolinite prisms and plates, while in the cloudy parts the incipient hydro-micas are more in evidence. Also in the cloudy areas knots and bunches of kaolinite sometimes occur, usually with a concentration of the limonite scum about them, as if it had been pushed out by the growing crystals. There are places too where this scum is puckered or drawn together about centers suggesting the contraction of a colloidal substance upon drying. The breccia-like structure seems due to a contraction in the clay not long after its deposition which formed irregular cavities or cracks. These were then filled through infiltration with purer material derived from the clay itself. The local variations in minerals noted in Section XIV may be

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explained as the metamorphic equivalent of these areas. The minerals in order of their importance here are (1) kaolinite, (2) hydro-micas, (3) quartz, (4) zircon, (5) tourmaline, (6) rutile, (7) mica.

The kaolinite is by far the most abundant, the lighter areas being made up of the small crystals of it.

The hydro-micas are present but do not show a marked development. They occur most often in radiate or fan-shaped groups of not more than 4 or 5 plates, each of which are seldom over 5 to 7 microns in diameter.

Quartz is scarce, as are also the other remaining minerals.

Section XVI.—"Semi-flint" clay from Woodland, Pa.[30]

Microscopically this resembles the "semi-flints" examined from other localities. It is of finer texture than No. XIV, but coarser than XV. Perhaps 90 per cent. of the section is visibly crystalline, kaolinite plates, prisms and fans with hydro-micas making up its bulk. Sharp sericitic plates are in evidence because of their higher index and interference colors. The section is considerably clouded by a scum of limonite.

Quartz grains are scarce. Rutile (?) needles (under 2 microns length) are present in large numbers and often grouped, suggesting the weathered residue from former biotite scales. Zircon grains were also noted but are not important.

The dehydration of two samples of Woodland clays gave the following results:

DEHYDRATION TESTS OF WOODLAND, PENNSYLVANIA, CLAYS.

	Per cent. loss at 112°	Per cent. ignition loss	Total per cent. loss
15 Mottled flint clay.....	0.39	13.3	13.7
14 "Soft clay".....	0.39	12.11	12.5
	0.58	12.1	12.7

The differences here are not so great as those shown by the Strasburg, Ohio, clays, but the amount of kaolinite seen in Section XIV was greater than that of the other semi-flint clays.

That No. XIV owes its lower water content to the develop-

[30] This clay comes from the same bed as do Nos. XIV and XV, but from a point about 1½ to 2 miles southeast.

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ment of hydro-micas seems probable since there is much of this mineral to be seen in the section, and greater amounts of quartz or other anhydrous mineral than in No. XV are not noted. The presence of hydro-micas up to 20 or 25 per cent. would produce about the reduction in dehydration loss here noted.

MT. SAVAGE, MARYLAND.

The fire clays are found outcropping toward the top of Savage Mountain and dipping steeply under its eastern slope. They are overlain by the Homewood sandstone of the Pottsville formation[31] which gives them a stratigraphic position similar to that of the Woodland, Pa., and Olive Hill, Ky., flint clays. This clay is underlain by a heavy conglomerate. The Mt. Savage coal is sometimes present above the clay[32] but in the mines visited by me no coal was seen.

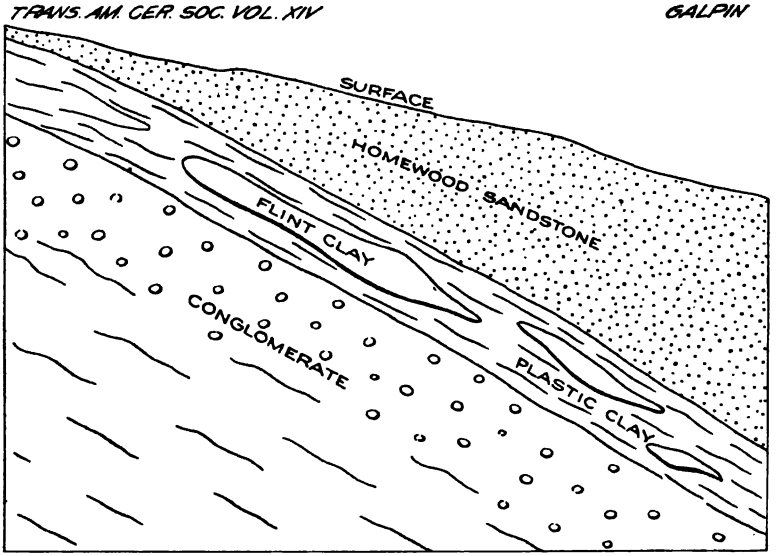

Fig. 6.—Section at Mt. Savage, Md.

The total thickness of clay shows a variation from 2 to 20 feet, made up of plastic and non-plastic material. The flint

[31] Md. Geol. Surv., Report on Allegheny County.
[32] Ries, Clays of Maryland, Md. Geol. Surv., IV, Pt. III.

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clay is found toward the middle of the bed, swelling and pinching with great irregularity. Frequently it is represented only by lenticular masses which may be separated from each other along the dip by a distance of several feet. The surfaces of these lenses are plainly marked with slickensides, giving evidence of considerable movement along them. The clay in the lenses is usually greenish gray, sometimes mottled and broken into irregular chunks by cracks or joints along which oxides of iron have been deposited. Conchoidal fracture is not well developed, and in general appearance this clay is not so flint-like as the specimens from other localities.

The plastic clay is of a lighter color and soft enough to be broken up in the hands. There are at times parts which are black, due to the presence of organic material. These are usually toward the top of the bed where coal is said to be found in some cases. The proportion of plastic to flint clay is higher than in most other localities, and as far as our observation goes, the plasticity of the soft clay is greater than that of the soft clay from other localities visited. Because of the geologic structure of the region the clay is unusually wet, a fact which may have a direct bearing upon the development of the plastic clay, and which will be discussed later.

Section XVII.—Flint clay, Mt. Savage, Md.[33]

When examined under the microscope this clay is similar to No. XVI from Woodland, Pa., Few well defined crystal grains exceed 30 microns in greatest diameter, although there are frequently areas 200 to 300 microns across through which are grown many more or less distinct plates in parallel orientation. Often the spaces between the parts of one such group of plates are filled by another set of grains in different orientation from the former but parallel to each other. Such structures may well represent two or sometimes more intergrown crystals although it is not thought that they represent twins, since there is no apparent crystallographic relation between the position of the two sets. These areas are so irregular that they prob-

[33] While called a flint clay this more closely resembles, both under the microscope and in the hand specimen, the "semi-flint" clays of other districts.

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PLATE IV.

Fig. 1.—Flint clay, Mt. Savage, Md., between crossed nicols. Shows development presumably by hydro-micas along a slip plane × 160.

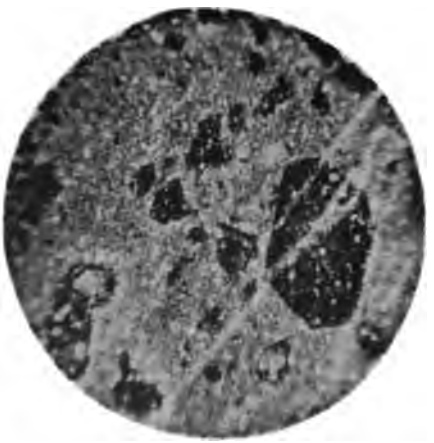

Fig. 2.—Semi-hard clay, Olive Hill, Ky., by direct light. Shows cloudy areas which may represent weathered feldspars × 80.

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ably are not caused by the weathering of feldspar grains in situ, but represent instead intergrowths of rather large crystals.

The section is crossed by several cracks, which evidently represent slipping planes, as indicated by the drag of the minerals along them (Plate IV, Fig. 1). These cracks must have served as passageways for solutions for the reason that they are usually tinted strongly by limonite.

The determinable minerals are (1) kaolinite in plates, prisms and fans, more commonly "ribbed" by the hydro-micas; (2) hydro-micas in individual flakes or grouped in fan-shaped aggregates. The areas described above are composed of hydro-micas. This mineral apparently makes up from 50 to 60 per cent. of the clay.

Minute rutile needles are abundant, small zircon grains common, but prisms of tourmaline and grains of quartz are rare.

Muscovite scales are also rather rare and seldom exceed 15 microns length. An unusual reddish mineral was noted along the slickensides in one or two instances, which may be eucolite or eudialyte. The evidences are not satisfactory for certain identification.

Section XIX.—Prepared from powder of plastic fire clay, Mt. Savage, Md.

The powder was found to be made up of individual crystal plates and grains not exceeding 20 to 25 microns diameter, while much of the material was too fine to determine. It is interesting to compare this powder with that of a flint clay, and for this purpose a section of the "flint" from Strasburg, Ohio, was prepared. It was made up of irregular, angular grains up to 80 microns diameter. As both clays had been ground the same length of time in a ball mill, this difference is suggestive, and probably shows why the "soft" and semi-flint clays develop greater plasticity than do the flint clays as they are more readily reduced to very fine particles, and furthermore the platy structures of these particles would develop greater plasticity than would rounded grains of equal mass.

Only one plate of kaolinite could be identified in this section,

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but a considerable amount of the material was shown to have an index of about 1.54 by the use of index liquids, which indicates the presence of more in the section.[34] The one referred to was strongly ribbed by hydro-micas. The hydro-micas are the most common minerals, showing indices above 1.554 and in some cases running up to above 1.58, which would indicate that the composition was approaching that of muscovite, scales of which are also common in the section.

Rutile and zircon are present, the former being more frequently seen.

Dehydration tests on the Mt. Savage clays afford results quite similar to those of the Strasburg clays.

DEHYDRATION TESTS OF MT. SAVAGE, MARYLAND, CLAYS.

	Per cent. loss at 112° C	Per cent. ignition loss	Total per cent. loss
17 Flint clay	0.67	11.72	12.4
18 "Semi-flint"	0.66	7.37	8.03
19 Plastic clay	0.87	6.33	7.2

It may be noted here that the Mt. Savage flint clay was compared microscopically with the semi-flints of other districts and the lower water content would seem to bear out the similarity. The "semi-flint" and the "plastic" clays show close agreement with similar varieties from Strasburg. The samples here tested were collected, as at Strasburg, ranging from the center of the clay bed toward the hanging wall.

OLIVE HILL, KENTUCKY.

The geology of this region has been described by Greaves-Walker[35] and also by W. C. Phalen.[36] The former has given such a detailed account of the occurrence of the clays that it seems necessary only to point out a few facts about the region. The following section from Phalen's report is characteristic:

[34] Quartz is also of about this index, but does not show the platy structure of kaolinite.
[35] Trans. A. C. S., Vol. IX, 1907.
[36] Bull. 285, U. S. Geol. Surv., Clay Resources of Northeastern Kentucky.

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SECTION AT OLIVE HILL, KENTUCKY.

	Ft.	In.
Coal	...	2–6
No. 3 clay	1–9	...
Drab-flint clay	1–9	...
Semi-hard clay	1–5	...
Pink ore	...	18–20
Blue shale	...	4–8
Iron ore	...	...
Top of lower carboniferous limestone	...	...

There is, of course, considerable divergence from this section. In the "Burnt House" mine, for instance, flint and semi-flint clays only are found, while the roof is a massive sandstone. At the same horizon, and but a short distance from some of the "Burnt House" workings, is found the peculiar clay described by Greaves-Walker as "Aluminite" rock. It seems that there must be a transition from this into flint clay although the mine workings are not reported to show it. It is also possible that it may represent a more or less distinct lens.

The Olive Hill clay is correlated with the Mt. Savage, Md., and Woodland, Pa., clays, and, hence, would be at the Mercer horizon of the Pottsville.

The samples examined represent (1) *a*, typical flint clay, *b*, top of flint clay bed; (2) the semi-flint; (3) the aluminite varieties described by Greaves-Walker. All are found in or near the Burnt House mine.

(1*a*) (Specimen No. 21) is of buff color and shows a good conchoidal fracture. Small concretion-like spots may be seen. It is very similar in appearance to some of the Clarion, Pa., flint clays. Fractures in this clay are frequently lined with small plates of barite.

(1*b*) (Specimen No. 20). This clay is darker than No. 21 and shows its resemblance to the typical flint clay.

(2) (Specimen No. 22.) A smooth buff-gray clay cut up into interlocking lenses by slickensides. The central parts of these lenses are like the flint clay.

(3) (Specimen No. 23.) The aluminite is a buff or pinkish

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rock of great toughness having a sharp but rough conchoidal fracture, the surfaces studded with oolites like those seen in bauxite, but of small size and seldom exceeding 1 mm. in diameter.

Section XX.—Clay from the top of the flint clay, Olive Hill, Kentucky.

Structurally this clay is similar to No. XI from Clarion, Pa. It is, however, richer in carbonaceous matter, which, along the cracks that served as pathways for solutions, had precipitated iron in the form of pyrite. Scattered through the clay are cloudy areas sometimes of circular outline and occasionally bearing remarkable likeness to the cross sections of feldspar fragments (Plate IV, Fig. 2). Crystallization of kaolinite prisms has formed clear patches in some of these areas, often producing radiate structures within, and more frequently about the periphery of the cloudy area (Fig. 7).

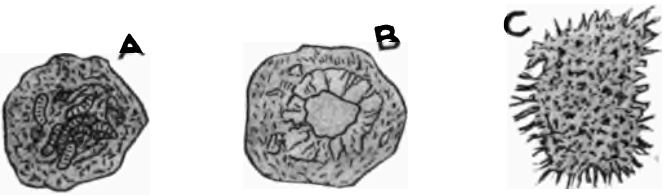

Fig. 7.—Types of structures characteristic of Olive Hill, Ky., clays.
a. An irregular mass of kaolinite prisms developed toward the center of a cloudy oolite.
b. Kaolinite grains or prisms producing radiate structure within oolite.
c. Radiating kaolinite crystals bordering an irregular clouded spot (possibly a weathered feldspar fragment).

Kaolinite is the most common mineral although hydromicas are to be seen, especially as ribs in the kaolinite.

Quartz, rutile, zircon and tourmaline are present in lesser amounts.

Section XXI.—Flint clay, Olive Hill, Kentucky.

This section closely resembles No. XX in mineralogical character, but is free from pyrite and contains much less carbonaceous material, and the structure is like that described in Section XI. There are traces of a sort of "mare's tail"[37] arrangement in the parts least crystallized. These structures are cut

[37] This term has been borrowed from meteorology where it is sometimes used to designate light wispy cloud structures.

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by the concretionary and cloudy areas. It is thought possible that these structures were formed by movements during contraction of the colloidal jel, of which the clay was largely composed, as some of the water was squeezed from it by the weight of accumulating sediments above. Traces of such structures are to be found in all of the very fine-grained flint clays.

Kaolinite prisms (up to 70 microns length) show a great variety of bent and contorted forms. "Ribbing" by hydromicas is a prominent feature and is apparently responsible for much of the warping in the kaolinite prisms. Muscovite is practically absent.

Quartz may be seen in widely scattered corroded grains up to 400 microns diameter. Other accessory minerals are as noted in other sections.

Section XXII.—Prepared from powder of semi-flint clay, Olive Hill, Kentucky.

This section shows largely individual plates, but also many aggregate grains, indicating that the development of hydromicas in this clay is not as complete as in some of the semi-flint clays from other localities, for the development of hydromicas seems to accompany any movements in the clay which tend to loosen up the individual plates, resulting in more complete disintegration into individual grains upon grinding.

The main mineral seen is hydro-mica. No kaolinite was identified, but is doubtless present to some extent.

Muscovite is not common, and the same is true of quartz and the other common accessories.

Section XXIII.—Highly aluminous flint clay, Olive Hill, Kentucky.[88]

Here one sees numerous concretions or oolites (Plate V, Fig. 1) scattered through a fine-grained ground mass, which is similar to that of Sections XX and XXI, but for fewer kaolinite prisms and occasional patches of mineral grains which show a higher index than kaolinite, and a structure differing somewhat from that of mica. Careful determinations of elongation, extinction and birefringence together with comparison to known hydrargyllite (gibbsite, $(Al(OH)_3)$ lead to the conclusion that

[88] The aluminite of Greaves-Walker.

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PLATE V.

Fig. 1.—So-called "Aluminite," from Olive Hill, Ky., by direct light. Shows structure of oolites × 80.

Fig. 2.—Section of "Aluminite" from Olive Hill, Ky., between crossed nicols. Shows hydrargyllite (gibbsite) recrystallized in central part of the oolite represented in Fig. 1 × 200.

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these bunches are composed of grains of that mineral (Plate V, Fig. 2). It is more common in the oolites than in the ground mass. Here it is seen in nucleal groups and concentric bands separated by rings of cloudy, extremely fine-grained material which may be a bauxitic mixture.

Kaolinite prisms are rare in the oolites but are closely associated with the hydrargyllite in the ground mass. The hydrargyllite may represent the recrystallization of hydrous alumina which was present originally in the sediments.

This clay seems to represent an intermediate phase between kaolin and bauxite.

Dehydration of the Olive Hill clays gave the following results:

DEHYDRATION TESTS OF OLIVE HILL, KENTUCKY, CLAYS.

	Per cent. loss at 112° C	Per cent. ignition loss	Total per cent. loss
21 Flint clay	0.82	13.2	14.0
22 Semi-flint	0.96	11.7	12.7
23 "Aluminite"	0.4	13.0	13.4

The "semi-flint" shows similarity in water content to the Mt. Savage "flint" and the Woodland "soft" clay.

The aluminite, despite the lower amounts of kaolinite to be seen, shows a fairly high water content due to the presence of some hydrargyllite ($Al(OH)_3$).

OTHER CLAYS EXAMINED.

For purposes of comparison, a microscopic examination was made of the following clays:

Missouri flint clay (ground section).
Washed kaolin from Quebec (prepared from powder).
Washed Delaware kaolin (prepared from powder).
Halloysite from Alabama (prepared from powder).
Indianaite from Indiana (prepared from powder).
Tennessee ball clay (prepared from powder).
Plastic New Jersey fire clay (prepared from powder).
St. Louis fire clay, hard (prepared from powder).
St. Louis fire clay, soft (prepared from powder).

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MISSOURI FLINT CLAY.

This is a cream-colored clay, having a fair conchoidal fracture and a more earthy luster than the other flint clays examined. The mode of occurrence has been briefly pointed out in the introduction to this paper.

Section XXIV.—Flint clay from Missouri.

This clay is structurally like Nos. XX, XXI and XI, but shows much greater development of the "mare's tail" feature (Plate VI). The texture is much finer than that of any other clay ex-

PLATE VI.

Section of Missouri flint clay between crossed nicols. Shows the mare's tail structure and the extremely fine grained crystalline texture X 300.

amined, there being comparatively few mineral grains of size sufficient for identification.

The minerals determined are (1) kaolinite prisms, occasionally somewhat "ribbed;" (2) minute scales of muscovite; (3) hydrargyllite (gibbsite) (?). Of this last mineral we cannot be certain as the grains were too small for identification. Their close resemblance to those seen in Section XXIII leads us to classify them as such, especially as the Missouri clays often show percentages of alumina higher than that of kaolinite.

Wheeler has noted in his work on the Missouri clays[89] that

[89] Mo. Geol. Surv., Vol. XI, 1897.

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the water content of the flint clays often exceeds that of theoretically pure kaolinite, and suggests that it may be caused by the presence of some mineral such as pholerite, or possibly by the admixture of kaolinite and bauxite. The latter view seems more probable from the examination of a single slide and also from the fact that of the hydrous aluminous minerals, only kaolinite, muscovite, hydro-micas, and hydrargyllite were identified in sections of several of the eastern flint clays.

WASHED KAOLIN FROM QUEBEC.

While the greater part of this powder is composed of very small particles there are numerous crystalline grains which sometimes reach lengths of 50 to 60 microns. Many of these grains are platy, with low index of refraction and the optical properties of kaolinite usually seen. Two or three well developed fans of the same mineral were noted, but it is probable that most of these fans that exist in the crude kaolin are broken up during the process of washing. A few good tourmaline prisms were seen and occasional flakes of mica.

A chemical analysis of this kaolin showed it to be of almost theoretical purity. Its loss on dehydration was 14 per cent.

WASHED DELAWARE KAOLIN.

The powdered material is seen to be composed largely of clear transparent plates, the largest of which are as much as 100 microns across. Their outlines are usually irregular but some are seen which are hexagonal. Some of the smaller grains are more fibrous than platy. When mounted in a liquid having a refractive index of 1.54 their edges become indiscernible, showing that the index of the plates is close to that of the liquid. The interference colors range downward from grays of the first order. Extinction is nearly parallel and in some cases quite so. A few of the plates are of a slightly yellowish color. No fan or prism-like aggregates were noted, but may be present in the kaolin as the process of mounting would tend to break them down. The mineral is doubtless kaolinite.

Some mica-like flakes are present, as are also numerous small fibrous bunches which show the properties of the hydro-micas. A few angular quartz grains were noted as well as some small grains taken to be zircon though not definitely identified.

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HALLOYSITE FROM ALABAMA.

Numerous platy grains are seen in the halloysite powder, but when viewed with magnifications of 600–800 diameters, these grains seem to be composed of many smaller ones, the optical properties of which could not be determined although they seemed to be weakly doubly refracting. Some small plates of muscovite were the only grains which could be identified with certainty. The refractive index of the unidentified material seemed to be above 1.554, suggesting the possible presence of hydrargyllite.

Upon dehydration the halloysite lost 15.5 per cent. of its original weight.

INDIANAITE.

The powder is mainly crystalline in plates and grains ranging from 80 microns down. The plates often show a roughly hexagonal outline frequently elongated parallel to one of the diagonals. They have but slight effect upon polarized light. There are also fans or bunches of plates which in many cases show the "ribbing" so characteristic of the prisms in the flint clays. The double refraction is a little higher than that usually ascribed to kaolinite, but the agreement of other properties favors this mineral.

Quartz and zircon grains are present and also a very little greenish mica. Some sharply angular fragments, possibly of opal, have been noted. About 60 to 70 per cent. of the Indianaite seems to be made up of crystalline kaolinite or a very similar mineral.

TENNESSEE BALL CLAY.

This powder is composed of apparently crystalline granules too small to identify (less than 1 micron diameter). A few grains are present which seem to be zircons. Much of the material has a refractive index of about that of kaolinite and very likely is that mineral.

NEW JERSEY FIRE CLAY.

This powder is of finer grain than that obtained from any of the semi-flint clays. No grains were seen to exceed 15 or 20 microns. The coarser grains are frequently platy and occasionally show roughly hexagonal outline. Their index is

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below 1.554, but was not determined more definitely than that. They are thought to be kaolinite. Quartz and zircon grains were seen as well as a few muscovite flakes.

HIGHLY ALUMINOUS FIRE CLAYS FROM NEAR ST. LOUIS.

These two samples were sent by the Laclede-Christy Clay Products Co., both being obtained from Missouri. They have the following chemical composition, as determined by R. T. Hipp, Ceramist.

	178	165
SiO_2	45.45	31.89
Al_2O_3	38.92	51.57
Fe_2O_3	1.42	1.17
CaO	0.1	0.63
MgO	0.32	0.34
Alkalies	0.83*	0.68
Water (combined)	12.35	12.99
TiO_2	0.49	0.49
	99.86	99.74

No. 178.—This is a hard gray clay (so-called flint clay) which, however, becomes plastic when ground.

The powder is composed of minute grains of crystalline appearance. The largest do not exceed 15 microns in diameter. Only a few grains could be determined among which were quartz in angular grains, mica scales and a few flat plates resembling kaolinite.

No. 165.—This is a soft clay, the sample examined being in small gray pellets, which are too hard to be crushed between the fingers.

Much of the powder is in a state of too fine division for purposes of identification, but there are numerous platy grains which sometimes measure 25 microns in greatest diameter. These grains are irregular or more rarely somewhat rhombic in outline. The refraction index is considerably above 1.54, and the birefringence is medium to high. Extinction seems to take place parallel to the diagonals of the rhombs, in which the longer diagonal is the direction of least elasticity. The

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prevalent angles in the rhombs are about 80°, although there is considerable variation from this angle.

It seems probable that these grains represent basal plates of hydrargyllite prisms.

The high percentage of alumina which the clay shows might in itself be taken as evidence of the presence of some hydrate of alumina, but if this excess is due to hydrargyllite the balance of the clay must be rather low in water content.

CHEMICAL TESTS.

Before making a microscopic examination of the flint clays it was thought that something might be learned concerning their constitution through their behavior towards acids. Accordingly several of the clays were powdered and digested with dilute H_2SO_4 for three hours. The residue was then filtered off and the iron and alumina precipitated with ammonia, filtered off, washed, ignited and weighed. Inasmuch as the iron present was never sufficient to more than tint the precipitate it was neglected. The precipitation was digested with HF, and again weighed, the figure last obtained being recorded as "soluble alumina."

The results are tabulated below:

Sample No.	1	21	22	23	4	Halloysite
% Al_2O_3 sol. in 15% H_2SO_4	9.57	7.84	15.66	27.44	4.44	31.1

1, Flint clay, Strasburg, O.; 21, flint clay, Olive Hill, Ky.; 22, semi-flint clay, Olive Hill, Ky.; 23, "aluminite," Olive Hill, Ky.; 4, flint clay, Missouri; halloysite, Alabama.

Exclusive of the "aluminite" and halloysite, the solubilities shown are proportional to the readiness with which these clays are reduced to individual grains.

Washed Delaware kaolin was similarly treated, using concentrations of 10, 15, 20 and 25 per cent. H_2SO_4.

Strength of acid	10%	15%	20%	25%
% soluble Al_2O_3	4.46	4.55	5.1	6.5[40]

[40] These figures represent the average of two determinations.

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It was concluded from these results and the microscopic examination that the solubilities in dilute H_2SO_4 are more an evidence of the fineness of the powders than of different mineral content except in cases such as the "aluminite" which has since been shown to contain $(Al(OH)_3)$ and the halloysite, the mineral composition of which could not be determined because of its fine texture.

These results may have considerable bearing on the value of sulphuric acid as a reagent for use in rational analysis.

It may be seen from the foregoing data that the assumption that kaolinite is the basic mineral of all highly aluminous clays is in a few cases incorrect, as in the instance of those "soft" or semi-flint clays in which the development of hydro-micas is greatest. No evidence has been found, in this investigation, pointing to the existence of any other hydrous aluminum silicates as important minerals in the purer clays although a rather wide range of materials has been included. The presence of alumina in excess of percentages allowable for kaolinite may frequently be attributed to the existence of hydrargyllite in a clay, and it seems possible that diaspore (Al_2O_3, H_2O) may also occur at times.

Comparison of the flint clays and their associates with other highly aluminous clays, shows that the main difference is in texture. In the flint clays the kaolinite crystals are knit together so tightly that when the clay is crushed they break out in aggregates rather than as individuals. In the semi-flint clays, the crystals though larger than in the flint clays are not so tightly interlocked and so become separated on grinding, producing some plasticity. In the plastic clays, the crystalline particles are smaller and at the same time more or less separated, due either to considerable disintegration of a once crystalline clay, or to a lack of any great amount of original crystallization. Kaolins differ from the flint clays in having crystallized under conditions of less pressure, allowing a more open structure, which may account for the fact that they are frequently less pure than the flint clays because of infiltration of foreign matter. Any attempt, however, to do more than point out general causes for differences in the various clays, must be based upon a most

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intimate acquaintance with all of the different deposits, which it has not been the writer's good fortune to acquire.

THE NATURAL HISTORY OF THE FLINT CLAYS.

The origin and the nature of the flint clays have always excited interest, and yet but few attempts have been made to explain why or how they come to be so different from the plastic clays.

E. Orton, Sr.,[41] Wheeler[42] and Hopkins[43] have advanced the view that the flint clays owe their hard and non-plastic character to part or complete crystallization of kaolinite in them. The soft, semi-plastic and plastic clays associated with them are considered to be much less crystalline and finer grained. The investigations described in this paper have led to a theory of formation which agrees only in part with these earlier views.

The land surface from which the clay-forming sediments of carboniferous times were derived was presumably rather low and traversed by sluggish streams. The rank types of vegetation which flourished are taken to be evidence of a warm climate, perhaps even subtropical in nature. The rocks which were being disintegrated and decomposed were mainly sedimentaries of Devonian and Silurian age. The weathering processes which were then active were more or less such as are active at the present time in hot moist climates, producing lateritic soils[44] which were richer in alumina and iron than soils of temperate climates.[45] As these soils were carried away by streams to be deposited in bogs, swamps or lagoons, part of their iron content was dissolved by carbon dioxide, resulting from vegetable decay in the water. As the sediments were laid down they became the soil in which the coal-forming plants flourished and here

[41] Geol. Surv. Ohio, VII, Part 1.

[42] Geol. Surv. Mo., XI.

[43] "Clays of Western Pennsylvania," Ann. Rept. Penn. State College, 1897.

[44] Lateritic weathering has been shown by many investigators to result in a reduction of silica, alkalies and alkaline earths and a concentration of alumina. See M. Bauer Neues Jahrb. Min. Geol., 1907, p. 33–90; Chaubard and Lemoine, Compt. rend., 146, p. 239–42. Others have found kaolinite to be formed also, E. C. Mohr, Bull. Dept. l'Agric. Ides. Neerld. No. 28; R. Lenz, Neues Jahrb. Min. Geol., 1909, II, 347.

[45] The deeply corroded quartz grains so frequently noted in the flint clays may be taken as a further evidence of lateritic weathering.

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they were further purified by the leaching action of plant roots and the carbonated waters of the bogs.

It may be pointed out then that the sediments of the clay beds must have been rather free from iron, calcium, magnesium, potassium, and sodium when laid down, due to their having been reworked and to the fact that the waters of the carboniferous streams were probably unusually high in their content of carbon dioxide. If we consider, further, that these clays usually served as soil in which coal vegetation was rooted, further purification is to be expected for it has been shown that plant roots are very active in removing lime, potash, and also magnesia, soda and iron to lesser content.

It then seems probable that when first laid down these clays were very fine grained, hydrous aluminous silicates with varying amounts of hydrous alumina as a result of the lateritic weathering. The amounts of impurities were probably as low as at present, when consolidation began, for it does not seem possible that there could be much circulation of leaching solutions through the settling clay mass.

Every fine-grained sedimentary deposit must include a large per cent. of water when first laid down, and this would be especially true of a clay bed. As soon, however, as any pressure was brought to bear the pore water would begin to filter out, carrying with it some soluble material. Eventually only enough water would remain to fill the spaces between the component particles of the clay provided no changes took place in these particles. Changes, however, do take place since the equilibrium of the surface weathering zone is not the same as that of the buried deposit. Recrystallization[46] then sets in, resulting in a compacting of the mass; and in some cases the excess water collects in fissures and cracks formed by the contraction attendant upon recrystallization. These fissures, under increasing load of overlying sediments, become filled by the squeezing in of fine particles and colloidal material along with the water. The brecciated appearance of the Woodland, Pa.,

[46] According to Doelter (Min. Pet. Mitth., XXVIII, p. 557–9) amorphous substances (such as colloidal $Al(OH)_3$, etc.) may be made to crystallize by digesting at 60°–70° with water. It seems quite probable that the heat produced by decomposition in the overlying coal or peat was sufficient to bring about recrystallization in the underlying clay.

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clay, and the dark waxy lenses frequently seen in other flint clays seem, in my opinion, to represent such changes. The filling material, as seen, usually contains fewer impurities than the surrounding clay. This may be explained on the ground that the small amount of alkali present, when the fine sediments were laid down, was taken up to form sericite and hydro-micas during the early stages of recrystallization. The hydrates of iron in the presence of a considerable amount of carbon dioxide formed siderite (as seen in Section VII); and it is of interest to note that sericitic scales are practically wanting and hydro-micas less common in this than in other flint clays due, it may be presumed, to the removal of the alkalies by the excess of carbon dioxide. When iron carbonate was not formed, most of the iron became enmeshed in the matte of growing crystals, remaining, as seen in many sections, as a sort of scum in the less altered parts of the clay. The fixation of these impurities left the material which filled the skrinkage cracks in a purer condition, so that on recrystallization a nearly pure kaolinite mass resulted. The noticeably white-burning character of the "dark" patches is explained on these grounds.

The crystallization of kaolinite and hydro-micas in the flint clays has gone on at about the same time as is indicated by the fact that many of the kaolinite prisms contain plates of the higher index mineral. From all the evidence I could gather through examination of numerous thin sections, there seems to be an isomorphous or nearly isomorphous series of minerals, ranging from kaolinite through to muscovite. Sometimes in a single prism there may be seen sections or plates whose optical properties vary between those of the aforesaid minerals as limits. Usually the plates of higher index are distributed through the central portion of a prism, indicating that the kaolinite continued to form after the available alkalies had been used in the growth of muscovite or the hydro-micas. There is not, however, any appearance of growth of the kaolinite at the expense of the micas. Hickling[47] has described kaolinite prisms from some of the English china clay deposits which show a variation from kaolinite to mica. He considers that there the musco-

[47] "China Clay, Its Nature and Origin," Trans. Inst. Min. Engrs., Eng. XXXVI, p. 10, 1908–9.

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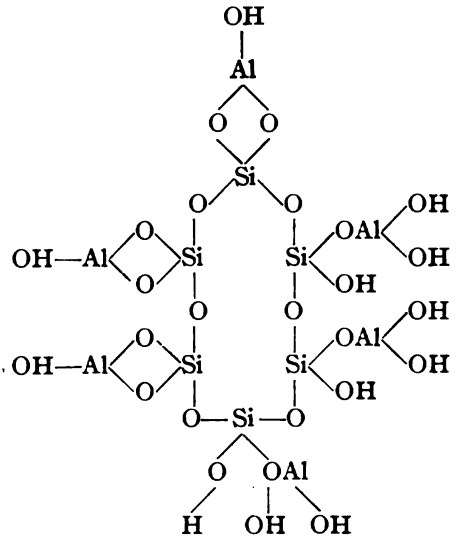
vite represents a transition stage in the weathering of feldspar to kaolin, which is doubtless correct.

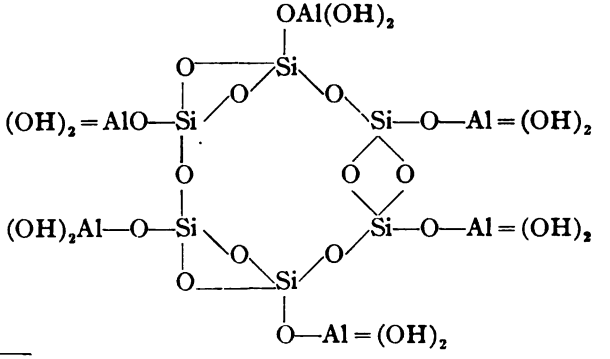
The apparent transition from sericite to kaolinite has been noted in other instances.[48]

Although the empirical formulae commonly used for the micas and kaolinite do not give great resemblance, it is possible to so construct them that they will show much similarity as follows:

Kaolinite $3(H_4Al_2Si_2O_9)$



Second Kaolinite Arrangement



[48] V. Selle, Chem. Cent., 1908, **11**, 1903.

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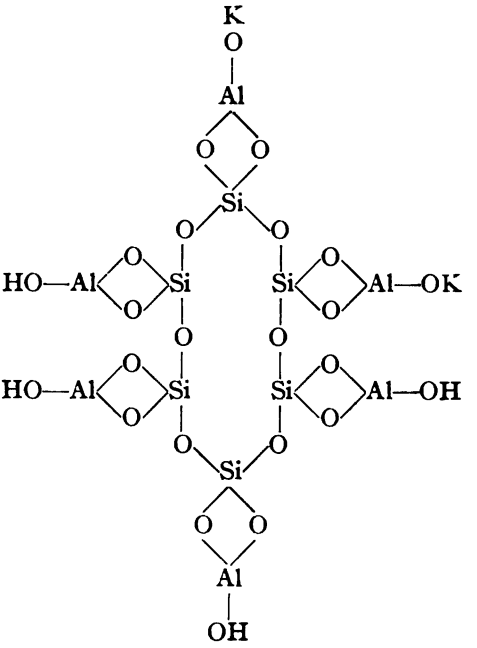
Muscovite $2(H_2KAl_3Si_3O_{12})$



Although such structural symbols are largely speculative, they are given because they are suggestive. The change from muscovite to kaolinite is accomplished through the replacement of two (KO) groups by two (OH) and the addition of $3H_2O$. In a molecule of the size postulated such an addition would not of necessity change either form or molecular volume to a great extent.

Mellor and Holdcroft[49] have classed muscovite chemically with kaolinite saying that in muscovite there appears to be an addition of three kaolinite groups where two (OH) are replaced by equivalent (KO) groups. They propose a formula for kaolinite, however, which joins all of the hydroxyl groups with the alumina thus:

$$\begin{matrix}(HO)_2 = Al - O.SiO \\ (HO)_2 = Al - O.SiO\end{matrix} \Big\} O$$

[49] "The Chemical Constitution of the Kaolinite Molecule," Trans. Eng. Cer. Soc., Vol. X.

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This arrangement is based largely on the fact that dehydration curves for kaolinite show no discontinuities of constitution.

Some other investigators have favored distributing three hydroxyl groups between both Si and Al. Among these are F. W. Clarke,[50] F. Hundeshagen,[51] W. Vernadsky,[52] G. Simmonds,[53] and W. Pukall.[54] P. Groth[55] and F. Ulffers[56] favor symbols similar to those of Holdcroft and Mellor.

The second kaolinite formula would conform somewhat to the ideas of the latter, but the objection is apparent that the substance should be hexagonal (trigonal) with such a symbol. In either case the possibilities of isomorphism between kaolinite and muscovite seem fair. On the other hand, it may be that isomorphism extends only to the complete replacement of K by H; and that with the addition of water a molecule is built up which, though not capable of forming isomorphous mixtures with the micas, is sufficiently similar to be oriented through contact with them. I am inclined to believe in complete isomorphism since the analyses of muscovites show considerable variation of hydrogen and alkali content, water frequently being present up to 6 or $6^1/_2$ per cent. often as an *addition* in part but occasionally *replacing* the alkali. To my knowledge, no mica has been reported in which the alkalies have been totally replaced, yet such an occurrence does not seem impossible or improbable except for the fact that alkalies are usually present to a slight extent where micas are forming. Such a mica would have the theoretical composition: $H_3Al_3Si_3O_{12}$, or in per cents., $H_2O = 7.5$, $Al_2O_3 = 42.4$, $SiO_2 = 50.1$.[57] There would then be two classes of micas showing water content in excess of the theo-

[50] "Constitution of the Silicates," 1896.

[51] Zeit. angew. Chem., Vol. XXI, 1908.

[52] Zeit. Kryst., Vol. XXXIV, p. 37, 1901.

[53] Jour. Chem. Soc., Vol. LXXXIII, p. 1449, 1903.

[54] Chem. Zeit., Vol. XXXIV, 610–13.

[55] "Tabellarische Uebersicht der Mineralien," p. 137, 1898.

[56] Jour. prakt. Chem. [2], LXXVI, p. 143, 1907.

[57] Brackett and Williams (Am. Jour. Sci., XLVII, ii, 21, 1891) have described a mineral which they call rectorite, having a theoretical composition of $H_2Al_2Si_2O_8$ (Al_2O_3 42.52 per cent., SiO_2 49.99 per cent., H_2O 7.4 per cent.), which is biaxial, strongly birefringent, with a refractive index *below* balsam (1.54). The properties of the hydro-micas are very similar to this mineral, except that the refractive index in them is considerably above that of balsam.

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retical amounts: (1) the hydrated muscovites in which the excess water is in the nature of an addition, and (2) the hydro muscovites in which the water replaces alkalies. It seems probable that both types are represented in the flint clays, when the first recrystallization had taken place in the presence of an excess of water and a want of sufficient alkalies for the formation of muscovite only.

It is therefore suggested that the consolidation of the largely colloidal sediments took place partly as the settling of a colloidal gel, but mainly as a recrystallization of their hydrous aluminum silicates, with the formation of minute interlocking crystals of kaolinite and hydrated micas, resulting in the formation of the flint clays.

During and after the "setting" of the flint clays there were forces at work tending to break them down. These forces were (1) pressure, both from the weight of overlying sediments and from compressive movements of the earth's crust, (2) heat derived partly from chemical changes that were taking place in the coal measures and in part from the friction of rock structures as they became readjusted to accommodate the changing pressures. The effect of heat and pressure on the flint clays was, first, to break up the outer parts of the bed with numerous fractures along which there was some slipping, and, second, to cause a dehydration and metamorphism of the parts so broken up. The extent to which this action was carried depended upon the local conditions. The Clarion clay bed was apparently affected but little, probably because of the massive sandstone strata above and below which protected it from unequal local pressures. The clays at the other localities show varying amounts of metamorphism. At Mt. Savage, where pressures were probably most active, the flint clays often occur only as lenses, the original bed having been broken across in many places by the local faulting. The usual irregular boundary between the "flint clay" proper and the more or less plastic clay associated with it is also readily explained by this view. The metamorphism which accompanied the fracturing and faulting resulted in the development of hydro-micas mainly, especially in the parts where movement and friction were greatest. That the kaolinite

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has lost part of its constitutional water, especially the smaller crystals, seems certain from microscopic examination of the "soft" and semi-plastic clays; and the results of dehydration tests show rather conclusively that the water content of some of the clays is close to the theoretical amount required for a pure hydro-mica.

The clays of this metamorphic type are known at various localities as "soft," "semi-hard," or "semi-flint" and "semi-plastic" clays. They show greater plasticity than the true flint clays because the crystal prisms have been broken down largely into plates and the clay as a whole made more friable by countless small faults, so that with equal amounts of grinding the metamorphosed clay affords much more fine-grained platy material which will develop some, although not great plasticity.[58]

The development of truly plastic clays from the semi-flint varieties has sometimes been accomplished through weathering. After much of the overburden was removed and the pressure on the clay beds reduced, the fault planes began to open, allowing water to enter and begin the process of breaking down some of the mineral grains, at the same time usually to deposit some iron and traces of lime, magnesia and alkalies in the numerous capillary fissures. The continuation of this process for a sufficiently long time has produced rather plastic clays, which are at the same time less pure than the unweathered clays. Such clays are found at Mt. Savage and also at Strasburg, and at each locality the overburden is thin. At Mt. Savage, the drainage is such as to facilitate weathering processes.

It may be of interest to consider somewhat the interpretation which may be made of results obtained by others in experimenting with flint clays.

Wheeler[59] gives the fire shrinkage of the Missouri flint clays as ranging from 9 per cent. to 14 per cent.

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[58] Cook ("Clay Deposits in New Jersey," p. 281), speaking of some kaolin clays, says: "Trituration, as rubbing between the fingers, breaks up the bundles and the mass is rendered thereby more plastic than in its original state." With the semi-flint clays the trituration was of a more rugged nature but equally effective.

[59] Loc. cit.

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Purdy[60] records fire shrinkages for Olive Hill flint clay as 9 per cent. at cones 9–11 and 13.

Knote[61] gives fire shrinkage curves for Olive Hill flint and plastic clays, Clearfield County (Pennsylvania) flint and plastic clays, Mt. Savage flint clay and others.

At cones 11–13 they run as follows:

Clearfield County flint clay	5 4%
Mt. Savage flint clay	5.6–5%
Clearfield County plastic clay	6.2%
Olive Hill plastic clay	9.4–9%
Olive Hill flint clay	9%

If the Clearfield County flint clay tested was of the type described in this paper as "soft" clay, the increasing shrinkage noted by Knote is found in clays showing increasingly fine and interlocking grains. The Missouri clay being of finer texture than any of the others fits in well at the end of the groups. However, the variability of texture possible in any locality makes it difficult to do more than suggest that the differences in shrinkage in the flint and semi-flint clays depend, first, upon the amount of colloidal material present, and, second, upon the size of grain and texture of the crystalline parts.

Knote found also that changes in specific gravity of flint clays upon heating differed from those in plastic fire clays, the semi-flint clays showing intermediate variations. He further found that kaolins behave in this regard very much as do the flint clays, a fact which accords well with our finding that crystalline kaolinite is the principal constituent of these clays.

The "soft" and "plastic" clays derived from the flint clays should show varying degrees of difference in their physical changes upon heating, depending mainly on the extent to which metamorphism has acted in dehydrating the kaolinite, and weathering in breaking down the semi-plastic clays.

The porosity curves given by Knote (*l. c.*) show a lower porosity at all temperatures for the semi-plastic clay than for

[60] "Pyrophysical Behavior of Flint Clays," Trans. A. C. S., X, p. 365–79.

[61] "Some Chemical and Physical Changes in Clays Due to the Influence of Heat," Trans. A. C. S., Vol. X. Knote examined several of the flint clays under the microscope but does not emphasize their crystalline nature. It seems probable that he worked with the powders, which do not give as satisfactory results as do the rock sections.

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the flint. This may be explained on the ground that the former have less constitutional water, and so upon dehydration would show less porosity, and that at higher temperatures their more micaceous nature would tend to reduce this absorption since Rieke[62] has found that muscovite cones become denser at cone 10.

It would seem also that the porous structures produced when the fragments of flint clay become dehydrated should make the material more refractory except in cases where gases containing fluxing elements come in contact with the clay.

Under such conditions it would seem that a less porous clay would have the advantage.

Those who are better acquainted with the uses of the flint clays may find other adaptations for the data obtained in this investigation.

SUMMARY.

From geologic occurrences, dehydration tests and microscopic examination the conclusions are drawn that:

(1) The flint clays have been formed by the setting and recrystallization of fine-grained largely colloidal sediments which have been purified mainly through the agency of carbon dioxide in the waters transporting and depositing them, and by the leaching action of plant roots. The products of recrystallization are mainly kaolinite, with minor amounts of hydrated micas.

(2) The "semi-flint" or "soft" clays have been derived from the flint clays through metamorphism by pressure and heat resulting in a conversion of much kaolinite into hydro-micas and the development of a completely microcrystalline structure of coarser texture than that of the original flint clay.

(3) The plastic fire clays associated with the flint clays have resulted from long weathering of the "semi-flint" or "soft" clays and are structurally more crystalline than the fire clays which have never been "set." They also differ from those clays in containing a high percentage of hydro-mica, kaolinite in all probability forming the base of other plastic fire clays.

[62] "The Effect of Muscovite upon Kaolin," Sprech., XLI, p. 577–83.

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(4) The change from muscovite through hydrated or hydromicas to kaolinite may take place without destruction of the original structure, indicating the possibility of an isomorphous series embracing all of these minerals.

(5) Knowledge of the microstructure and composition of a clay may be used to explain and predict peculiarities in its physical and chemical behavior.

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A SIMPLE ROPE HAULAGE FOR SHALE.

By W. A. HULL, Richlands, Va.

INTRODUCTION.

The problem of converting the raw material to a brick plant is usually not difficult or complicated. Nevertheless, it is one of the problems of brick making and one which must be solved individually for each plant, according to the various conditions existing, including the condition of the pocketbook. In some cases, what seems best at the start, and perhaps is best at that time, needs to be changed later on to meet altered conditions. That was the case with the Richlands Brick Corporation.

THE OLD HAULAGE SYSTEM.

The plant is situated on level ground just beyond the slope of the hill from which the shale supply is obtained. This shale bank was opened up some years ago at the point nearest the factory, and has been worked, for the most part, along the lines of least resistance. This resulted, eventually, in a bad lay-out and high operating cost. In order to get the tram cars high enough above the dry pan to put the shale in the pan by gravity and at the same time provide a shale storage for rainy days, the tram track was brought into the factory building over a trestle which gave the dumping place an elevation about twelve feet higher than track level on the flat ground between the factory and the shale bank. The tram cars were drawn up this incline by means of a wire rope and drum. From the foot of the incline, the ground slopes gently upward for about two hundred and fifty feet to the point, near the foot of the hill, at which the shale was first worked. Naturally the cost of getting the cars back and forth from the shale bank to the foot of the incline was small in the beginning, because the distance was short.

It was found, however, that the outcrop shale was better than that deeper in the hill and that the best way to work the shale was to skirt along the foot of the hill on a line making an angle of about 70 degrees with line of the track from the factory to the first working place. As the width of the workable bank was not great, the progress of the work increased the haulage

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distance rapidly. The bottom was allowed to rise gently so as to provide drainage and keep the grade of the track such that a loaded car would run out, and down to the foot of the incline, by gravity. A man or big boy was required to run the car out to keep it from going too fast in places and wrecking and to stop it at the foot of the incline. Then a mule was required to pull the empty cars back to the bank and a boy to ride the mule down to get them. The distance became greater and at the same time the tonnage of shale used was increased until it became necessary to put on another mule and mule boy. By that time the length of the tram road was nearly 1,000 feet, and the factory was using from eighty to one hundred cars of $1^1/_2$ yards capacity per day. The haulage pay-roll was as follows:

Drum man (contract) say	$1.75	
Car rider	1.50	
Two mules	2.0	
Two boys	1.00	$6.25

THE NEW SYSTEM.

The cars in use were of the revolving type and heavily built. One empty was enough for a mule to pull up the grade. Doubtless we could have reduced the haulage cost to some extent by substituting lighter cars with good brakes, so that one man with one mule could handle two or more cars at a trip from the shale bank to the foot of the incline and back. But we had the drum and the engine; and it seemed like a reasonably simple matter to make the machinery do all the work, with an endless rope to the shale bank. This was decided upon some months before the second mule became necessary, but some time was required to work the bank into such shape that we could cut out the meanderings of the old track. When this was accomplished, there remained but one curve, and the track was in very fair shape as shale tracks go.

In order to pull in loads and return empties on a single track, keeping the rope on rollers as far as possible and at the same time avoiding extra work and delay at the dump, we had to make the drum reversible. This drum is a good substantial specimen of the hoisting drums commonly in use in brick plants for pulling cars up to the dumping place. It is friction-driven,

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the pulley shaft being belted to an independent 10″ × 16″ slide valve engine. At each end of the drum the flange carries a friction rim to engage a friction on the pulley shaft. This gives a proper distribution of the strain on the drum shaft. The bearings in which the drum shaft runs act as eccentrics and each is controlled by an arm or lever. These two levers are connected by a cross bar. Originally, the frame carried the pulley shaft on one side of the drum and brake shoes at the other. We took off the brake shoes and put in a second driving shaft with frictions and pulley. There were two pulleys on the engine and we connected the new driving shaft on the drum frame with the unoccupied engine pulley by a crossed belt. The engine runs continuously and the drum is now run either forward or backward by pressing it against one or the other of the two sets of frictions. When standing midway between the frictions, the drum is out of gear.

A bullwheel, consisting of an idle pulley running on a vertical shaft in a home-made frame, was placed near the shale bank end of the tram road. The rope would be more out of the way

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if the idler were under the ties, but at the start it seemed best to put it in in the easiest way and to have it up where it could be got at.

The rope extends from the drum to the terminus in two parallel lines, one between the rails and the other over the ends of the ties. Rollers are placed at intervals along these two lines to carry the rope. Curve sheaves with chilled wheels and cast stands were purchased to carry the inside rope at the curve. For the outside line we made sheaves by bolting two old car wheels together, flanges outward, making loose pulleys. These are set up on vertical shafts and do the work very well.

The equipment that had to be bought for the rope haulage is shown in the following list. The prices do not include freight. In addition to this list there are some few items, not large as to original cost, that should be credited to an unsightly but highly esteemed scrap pile.

EQUIPMENT PURCHASED.

2000′ $^5/_8$″ cast steel wire rope	$115.16
6 chilled sheaves with 17″ stands	21.30
10 No. 2 incline rollers and boxes	26.00
50 gum wood rollers 6″ × 12″ with wood bearings	14.00
12 $^5/_8$″ wire rope clamps	1.44
1 piece 2$^1/_2$″ shafting 6′ long 2 paper frictions 2 boxes	26.00
1 10″ × 10″ wood split pulley	1.98
55′ 8″ 6-ply canvas belt	23.76
1 6″ electric gong	5.75
25 No. 4 porcelain knobs	0.25
9 dry batteries	2.25
2000′ No. 10 galvanized smooth wire	1.87
	$239.76

This sort of haulage was new to all of us, so we expected some trouble at the start. Our expectations were abundantly fulfilled. However, the first attempts were timed to come in the dull season and were not as expensive as they would otherwise have been. And we had the advantage of being able to reinstate the mule on short notice. We could try the rope, discover something more to be done and then go on hauling the old

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way until we were ready to try again. This gave us a chance to avoid paying the full penalty for our inexperience.

One thing, we entirely overlooked. A rope wrapped on a single drum takes the form of a spiral, and as the drum winds the rope from one side and unwinds it from the other there is a travel of the rope across as well as around the drum. If the drum were long enough and large enough, the rope could go its course without interference; but with our little drum and 1000′ of haulage this was out of the question. So we placed an idle drum or spool under the pulling drum and parallel to it and ran the rope around both. This, I believe, is regular endless rope practice but we did not know it at the time. We find that three wraps of the rope around the drum is ample.

At first we had trouble with slipping and put extra lagging on the drum with grooves in the lagging. Later, when we renewed this lagging, we found that very slight grooves simply to give the rope a definite path were sufficient. The essential safeguard against slipping seems to be to take care of the slack in the rope. The proper way to do this is to have a weighted car on an incline and have the rope pass around a drum on this car. This will automatically take care of the slack and give a uniform tension in the rope. In adapting our old equipment we could not conveniently put in such an arrangement, so we left it out. We regulate the length of the rope as it changes with temperature conditions by throwing it in or out of one or two of the outside sheaves at the curve. Any further adjustment is made at the bullwheel at the end of the line. We secure a constant tension by means of the sag of the outside rope, which at the factory end is carried on rollers placed high and far apart. This seems to answer the purpose very well.

On one side, the rope runs the entire course between the rails. This makes it easier to keep the rope on rollers and minimizes the wear. The inside curve sheaves had to be placed a little outside the center of the track on account of low bearings on our old cars which would otherwise have struck the sheave stands. For some time we had trouble on account of the rope coming out of the sheaves. We still have the rope fastened to the car a little to one side of the track center on this account. No grip is used,

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so far, but a rigid iron ring is secured to the frame of each car and a tee on a chain about twelve inches long is slipped through this ring to make the fastening. This short chain has a play of about two feet along the rope, between two wire rope clips that act as stops. This play gives the mule boy something to go and come on in spotting his car over the hitching place.

For some time we had trouble at the curve due to the rope coming out of the sheaves. The load would come down around the curve with some slack in the rope ahead of the car, and if the rope were out of one of the sheaves there was a fair chance that the slack rope and dangling chain would loop around that sheave with disastrous results. Wooden approaches or guards—simply a sloping piece of plank to carry the rope over the sheave without catching—have done away with this trouble. The rope sometimes comes out of a sheave but on the return trip the car invariably threads it in again. We do not regard the curve as a desirable thing, but it is no longer a source of trouble.

With a given engine speed, the speed of the rope can of course be regulated by the size of the pulleys and frictions between the engine and the drum. As we have it arranged, the empty cars make the trip of approximately 1000′ in about one minute and fifteen seconds, or at the rate of about nine miles an hour. The loads come in in about two minutes or about 5.7 miles an hour. Both speeds could be increased somewhat but in our case it is not necessary. At this speed the engine will pull two heavy cars each loaded with $1^1/_2$ yards of shale up the incline together; allowing two minutes for shifting cars at bank and two for dumping, a round trip can be made in $7^1/_4$ minutes. This would make 82 trips or 246 yards in ten hours. That is about twice what the factory uses, so there is a liberal allowance for the inevitable little delays. Furthermore, our present cars will be replaced with new ones of three or four yards capacity, built low and dumped at a self-dumping tipple. This will shorten the time required for dumping and for shifting at the bank.

We are still in the experimental or developmental stage with this haulage. For the present the pay-roll for operation may be taken as follows:

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Drum man	$1.75	
Mule	0.50	
Boy	1.00	$3.25

We rate the mule at only 50 cents because his work is light and he is growing younger on short rations. On the face of it, this represents a labor saving of $3.00 per day or about 7 cents per thousand brick. However, the additional expense of up-keep and power will offset a considerable portion of this saving. There is also an added risk of break-downs.

As soon as our shale workings get into more regular material so that we can concentrate the loading and bring all cars to practically the same place, we expect to provide the car boy and the mule with permanent employment elsewhere. We have another place in view for the drum man as well, but we cannot see our way clear to take him away for the present.

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SOME POSSIBLE DEFINITE RELATIONS BETWEEN COMPOSITION AND PROPERTIES OF CLAYS.

By F. F. Grout and H. H. Brown.

INTRODUCTION.

Hundreds of analyses of clay have been made for the sake of estimating the availability of that clay for various uses. The resulting estimates are not very reliable. Many efforts have been made also to correlate the composition, and behavior—some of them quite noteworthy—but it is a common thing for the clay expert to ignore entirely the use of analyses.

Bischof's formula for fusibility and its rather wide use indicates a relation between composition and fusibility, though the physical condition and state of combination of elements have further effects, and the formula is discredited. The color of the clay and its burned products are intimately related to the elements present, but again the state of combination of the elements is so variable that men of experience hesitate to predict the color to be expected. The other physical properties of raw clay, such as plasticity, tensile strength and slaking, certainly cannot be related definitely to the elements present. The constitution, or state of combination of elements is probably responsible for plasticity, but this is not to be confused with composition. Kaolinite may or may not be plastic.

It occurred to the authors that the state of combination of the elements in raw clay largely disappeared in the process of vitrification, and that it was in a study of the burned ware that the most definite relationships would be found.

Let us review in brief the three stages usually noted in the burning of a clay. A common clay consists of several minerals of varying fusibility, and at incipient fusion enough of the most fusible minerals have been melted so that on cooling the glass binds the product firmly together.

At vitrification more minerals have melted and the liquid part has dissolved enough of the less fusible minerals that the viscous liquid nearly fills the pores between the particles that remain unfused. Now when this cools and the liquid becomes glass, or slag, the strength, harness, toughness, brittleness,

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etc., of the product depend much more on the part that fused than on the unfused matrix which preserved the form. Two paving bricks, equally well vitrified, may not be equally strong, hard, and tough, because of the difference in composition of the glass.

EXPERIMENTS.

We thought that melts could be made to test the quality of glass such as would be formed by the fusible minerals of clay. Simple mixtures were planned for the first tests; later ones to include more complex tests, and those in which kaolin was added to a proportion no longer capable of thorough fusion. Results here offered are only preliminary and the contribution is slight, but it is hoped that they are definite enough to encourage any one favorably situated to continue the work.

The mixtures melted and tests used on the slags were as follows:

1	CaO	37%	SiO_2	63%	Selected as most fusible, and then mixed with 10% $NaKCO_3$ to make more fusible.
2	FeO	54+%	SiO_2	46—%	
3	CaO	18%			
	MgO	20%	SiO_2	62%	

Fusion was effected in a fire clay crucible. The melt was poured into graphite-clay molds which were heated in preparation and cooled slowly in a muffle furnace after the melt was poured. Rapid cooling was thought to be injurious to the strength of the glass. The bar, about $^1/_2'' \times {}^1/_2'' \times 3''$, was broken in a transverse test. One piece was tested for hardness by comparison with Moh's scale. The other was tested in a piece of apparatus designed to show brittleness. A weight of 73 grams was dropped from successively higher and higher positions onto the bar of slag until it was shattered.

The viscosity of the melts, which is undoubtedly of importance in the degree of possible vitrification of a clay, was not measured, and did not seem to vary a great deal.

The hardness of the slags was 7 in each case. The modulus of rupture was greater in the iron slag than in the calcium slag, although the calcium slag had cooled rather faster; and in the calcium-magnesium slag, the strength again was high.

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The brittleness varied in a rather more pronounced way, the necessary drop for the calcium slag being only 8 inches, while that for the iron slag was 21 inches and that for the calcium-magnesium slag was 44 inches.

CONCLUSION.

In practice we know that excellent vitrified products are made from clays with a rather high proportion of potash, and some with considerable iron, but no very good vitrified products are made from high calcium clays. Thus far the results indicate a very definite relationship.

DISCUSSION.

Mr. Purdy: I congratulate Mr. Grout on this unique research. It strikes right at fundamental principles. I would like to know how much glass Mr. Grout thinks is formed in a vitrified paving brick, and if there is any regularity in the proportion or character of glass in paving bricks generally.

Prof. Grout: I have always thought of the porosity of materials as 25 per cent., and this 25 per cent. when filled with glass determines the product—it is fairly certain, but I have not tested it out so far.

Mr. Purdy: In that same connection, how would you explain the fact that some bricks are at the maximum strength when they have a porosity of 4 per cent., and some are not.

Prof. Grout: I explain that by the fact that the glass, which before vitrification is complete has one composition, has later absorbed the kaolin, or some other component, whatever it may be. By the time vitrification is complete the original composition has changed.

Mr. Purdy: Then is it a question of quality as well as quantity of glass formed?

Prof. Grout: Both, and increase of heat. Four or five hours would be sufficient to absorb the material that would decrease the strength of your brick—in a few cases.

Mr. Purdy: Can we expect that this glass would *decrease* in strength by *increase* in the solution of *the more refractory* substances in the clay?

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Prof. Grout: Yes in the few cases where that occurs.

Mr. Purdy: Most all paving brick clays are over-burned if vitrified beyond a certain porosity. It is almost impossible to burn a brick to a complete vitrification without very largely decreasing its abrasive and impact strength, and there is no regularity in the amount of porosity bricks have when burned just to their maximum toughness. I am interested to know which of the materials in a clay would cause this decrease in the strength of the bricks by being taken into solution by the glass.

I don't doubt the argument that Prof. Grout is making but I am quite curious to know how he will account for decrease in the strength of the glass by the solution of the more refractory materials of the clays.

Prof. Grout: There is no available evidence that addition of aluminium silicate to the glassy matrix of vitrified wares has a beneficial effect on strength. It may sometimes have the reverse effect.

Prof. Staley: In this connection I wish to call attention to the fact that some interesting data on the relation between composition and strength of glasses is to be found in the book "Jena Glass," by Hovestadt (see chapter on "Mechanical Properties of Glass"). According to this, high calcium has a detrimental effect on the strength of glass. That high calcium is detrimental to the strength of an enamel is held to be true by many enamel makers, especially those of Germany. Prof. Grout's finding that high calcium produced weak glasses is thus upheld by observations on two diverse kinds of glass.

The loss of strength in a brick when burned beyond a certain porosity is, in my opinion, more probably due to the development of vesicular structure than to a change in the composition of the glass.

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EXAMPLES SHOWING THE USELESSNESS OF RATIONAL ANALYSIS OF CLAYS AS A MEANS OF CONTROLLING GLAZE FIT.[1]

By Ross C. Purdy.

INTRODUCTION.

In our last Transactions[2] I made two assertions in the closing paragraph of an earnest discussion on this same topic. The first assertion was that the assumptions underlying the so-called rational analysis are not in keeping with the facts. The second assertion was "that the results obtained do not justify the claims which have been made as reasons for adoption of these analyses by the clayworker." This present article will be devoted wholly to the bringing forward of proof in the support of the latter, which, to the clayworker, is really the more important of these two assertions.

At the outset let me draw attention to the fact that the writer has never denounced either the ultimate or rational analysis as being wholly without value. This could not, with consistency, be the case for data obtained by these analyses have been used by the writer to good advantage in so many instances when considering fundamental problems as to make such a denouncement untenable. The writer's claim now is and always has been confined entirely to the application (and hence their value) of these analyses by the clayworker to the selection of clays, or the substitution of one clay for another in the compounding of body mixtures.

INVESTIGATION.

The present investigation was made with the class of 1912, Ceramic Engineering Department, The Ohio State University, as one part of their work on whiteware bodies. Each student was given a ball clay with which to make four body mixes; hence we had thirteen series of four bodies each.

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[1] Contribution from the Ceramic Engineering Laboratories of the Ohio State University.

[2] Trans. A. C. S., Vol. XIII, page 200.

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The composition of the bodies were those represented by the corners of the parallelogram A B C D, which the writer had used[3] in describing the limits of variation in composition of China and C. C. bodies. In percentages, these compositions are given in the following table:

TABLE I.

	A	B	C	D
Feldspar	20	20	8	8
Flint	40	28	40	52
Clay	40	52	52	40

The materials used were: Ohio silica flint; Canadian feldspar; Dillsboro kaolin; ball clay (thirteen different brands).

The batch for each body was 20 pounds, the ball clay constituting 20 per cent. of the entire batch in each case.

The ball clays used were as follows: Mandle-Sant, Tenn. No. 2. Mandle-Sant, Tenn. No. 3. Kentucky, source unknown positively, but probably not from the Kentucky Construction & Improvement Co. It resembles the Paducah clays. Mandle-Sant, Tenn. No. 5. Mandle-Sant, Tenn. No. 1. Mandle-Sant, Tenn. No. 9. Johnson-Porter, Tenn. No. 9. Johnson-Porter, Tenn. No. 10. English No. 12, source or agent not known. M. M. English, Moore & Munger. English, Hammill & Guillespie.

Procedure.—The ball clays were crushed in rolls, the body mixtures weighed, the weights in every case being checked by one of the instructors. The bodies were then blunged in Bonnot ball mills for twenty minutes, passed through a 100 mesh sieve, and then thickened to a plastic condition by allowing them to stand in frames on muslin-covered slabs.

Trial pieces of various sorts were then made for studying the several properties of the burned ware. For glaze fit, the trial pieces were 10 centimeter discs, which had been cut out from slabs of thoroughly wedged masses. Separate sets of three discs each were biscuited at cones 3, 6, 8, 10 and 12, respectively.

[3] Trans. A. C. S., Vol. XIII, page 92.

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The glaze used was the same as described last year.[4]

The glost heat treatment was cone 4 in 24 hours.

CLASS REPORT ON RESULTS.

The report of the glaze fit committee[5] is here given. At the time of writing this report the students did not know what ball clays had been used, and the instructors did not have analyses of them.

Tabulation of Results: The results obtained in glaze fit have been tabulated in Table A. C and F denotes craze and shiver respectively. The numerals 1, 2 and 3 denote roughly our judgment of the degrees to which the defect is manifest. The initials (H, F, D, etc.) are those of the students who made up the bodies. The letters A, B, C and D stand for the respective four corners of the parallelogram representing composition (as before described).

Results Shown in Curve Form: The results are shown graphically in the following curves. A base, or datum, line was established for each body mixture. A point on the datum line indicates perfect fit on all three of the trial pieces which had been biscuited at the cone indicated. Points above the datum line indicate crazing; those below, shivering.

The distances above or below the datum line, which represent the extent of manifestation of crazing or shivering, were calculated as follows: If all three trials were crazed to a degree indicated by 3 in the tabulated data, this would represent the worst possible case and the ordinate would be taken as 10. If two were crazed o the degree represented by the numeral 3 (an unusual case) the ordinate would be $6/9^6 \times 10 = 6.67$. If one was crazed as indicated by 2, one was crazed as indicated by 1, and the other was perfect, the ordinate would be $\frac{2+1}{9} \times 10 = 3.33$. In cases where only two trials were recorded, the denominator was reduced to 6, because (3 + 3) or 6 represents the worst possible condition. For shivering, the procedure was identical save that the ordinates were laid off below the datum line.

Discussion: The fit of the glaze on Body A of all members of the class was uniformly good with a tendency on the part of over half the trials toward a slight crazing at cone 12. As the composition of A was not far from Hecht's craze area for cone 10, and as the class 1911 found that the craze area ex-

[4] Trans. A. C. S., Vol. XIII, page 158.

[5] Roy Thompson and George E. Middleton.

[6] The numerator of this fraction is the value of the committee's estimate of the degree of crazing. In this case two trials show crazing of the degrees 3, hence, 3 + 3 or 6. The denominator is the value which would be obtained of all three trials crazed to the degree represented by 3. In this case, 3 + 3 + 3 or 9.

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TABLE A.—GLAZE FIT.

G. M.

Cones.	3	6	8	10	12
Body	Con.	Con.	Con.	Con.	Con.
A	F	F	F	F	C 1
	F	F	F	F	C 1
	F	...	F	F	...
B	C 1	C 1	F	F	C 3
	F	C 1	F	F	C 3
	F	...	F	F	...
C	F	F	F	F	F
	F	F	F	F	F
	F	...	F	F	...
D	F	F	F	S 1	S 3
	F	F	F	S 1	F
	F	...	S 1	S 1	...

B.

Cones	3	6	8	10	12
Body	Con.	Con.	Con.	Con.	Con.
A	F	F	F	F	F
	F	F	F	F	F
	F	F	F	F	F
B	F	F	F	F	C 3
	C 1	F	F	C 1	C 3
	C 1	C 1	F	C 1	C 3
C	C 1	F	F	S 1	S 1
	C 1	F	F	S 1	S 1
	C 1	F	F	S 1	F
D	F	F	S 2	S 3	S 2
	F	F	S 1	S 3	S 3
	F	...	S 1	S 3	...

C. P.

A	F	F	F	F	C 1
	C 1	F	F	F	C 1
	F	F	...	F	C 1
B	C 1	C 3	F	F	C 1
	C 1	C 1	F	C 1	C 3
	C 2	C 1		F	C 3
C	F	F	F	F	F
	C 1	F	F	F	F
	C 1	F	...	F	F
D	S 1	F	F	S 2	S 2
	F	F	F	S 1	S 1
	F	F	F	S 2	...

M. V. P.

A	F	F	F	...	F
	F	F	F	...	F
	F	F	...	...	F
B	F	F	C 1	...	C 3
	F	F	C 1	...	C 3
	F	C 1	...	...	C 3
C	C 2	F	F	...	F
	F	F	F	...	F
	C 2	F	...	...	F
D	F	F	F	...	S 1
	F	F	F	...	F
	F	F	...	...	F

F. A.

A	F	F	F	F	F
	F	F	F	F	C 1
	F	F	F	F	C 1
B	C 2	C 1	C 1	C 2	C 3
	C 2	C 2	F	C 1	C 3
	C 2	C 2	F	C 1	C 3
C	C 1	C 1	F	S 1	F
	C 1	F	C 1	S 1	S 1
	C 1	C 1	C 1	...	F
D	F	S 1	S 1	S 3	S 1
	S 1	S 1	S 2	S 3	S 2
	S 1	S 1	S 1	S 3	S 1

W.

A	F	F	F	F	F
	F	F	F	F	F
	F	F	F	F	C 1
B	F	C 1	C 2	C 2	C 3
	C 2	C 2	F	C 1	C 3
	F	C 2	C 2	C 1	C 3
C	C 1	F	F	C 1	F
	C 1	F	F	F	F
	F	F	F	F	F
D	F	F	F	S 2	S 2
	F	F	F	S 2	S 2
	F	F	F	S 2	S 2

F = fit, C = crazed, S = shivered, Con. = condition.

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TABLE A.—(*Continued*).

L. A. S.						H. K.					
Cones	3	6	8	10	12	Cones	3	6	8	10	12
Body	Con.	Con.	Con.	Con.	Con.	Body	Con.	Con.	Con.	Con.	Con.
A	F	F	F	F	F	A	F	F	F	F	F
	F	F	F	F	C 1		F	F	F	F	F
	F	F	F	F	F		F	F	...	...	F
B	F	C 2	C 2	F	C 3	B	F	C 1	F	F	C 3
	F	F	C 2	C 1	C 3		F	C 1	C 2	C 1	C 3
	F	...	C 2	C 1	C 3		F	C 1	...	...	C 1
C	F	F	F	F	F	C	F	F	F	S 1	F
	C 1	F	F	F	F		F	F	F	S 1	F
	F	F	F	F	F		F	F	...	...	F
D	F	C 2	F	F	F 2	D	F	F	F	F	F
	F	C 2	F	F	F		C 1	F	F	F	F
	F	F	F	F	F		C 1	F	...	...	F
G. F.						R. E. T.					
A	F	F	F	F	F	A	F	F	F	F	C 2
	F	F	F	F	C 1		F	F	F	F	F
	F	...	F	F	C 1		F	...	F	F	...
B	F	F	C 1	C 2	C 3	B	C 2	C 2	F	C 1	C 3
	F	C 1	C 1	C 2	C 3		C 1	C 2	...	F	C 3
	C 2	C 1	C 1	C 2	...		C 1	...	...	C 1	...
C	C 2	F	F	F	F	C	C 1	F	F	F	F
	C 1	F	F	F	F		C 1	F	F	F	F
	F	F	F	F	F		C 2	...	F	F	...
D	F	F	F	F	F	D	F	F	F	F	F
	F	F	F	S 1	F		F	F	F	F	F
	F	...	F	S 1	F		F	...	F	F	...
H. F. D.						L. C.					
A	F	F	F	F	F	A	F	F	F	F	F
	F	F	F	F	[illegible]		F	F	F	C 1	F
	F	...	F	F	...		F	...	F	F	...
B	F	F	C 1	C 1	C 3	B	F	F	F	F	C 2
	C 1	F	C 1	C 1	C 3		F	F	F	C 1	C 1
	C 1	...	F	C 1	...		F	...	C 1	C 2	...
C	F	F	F	F	F	C	F	F	F	F	F
	C 1	F	F	F	F		F	F	F	F	F
	F	...	F	F	...		C 1	...	F	F	...
D	F	F	F	S 3	S 1	D	F	F	F	S 1	S 1
	F	F	S 1	S 1	S 2		F	...	F	S 1	S 1
	F	...	S 1	S 1	...		...	...	S 1	S 1	...

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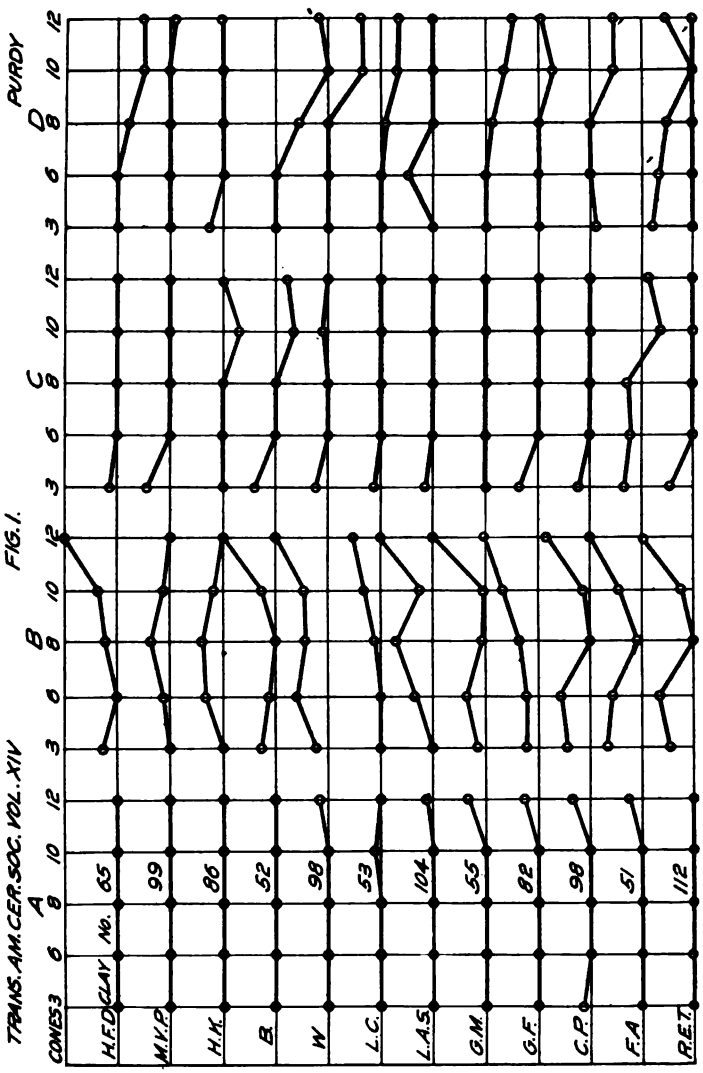

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panded at the higher cones, these results were more or less consistent. However, it is Body B which affords best opportunity for discussing crazing.

The statement by Professor Purdy[7] regarding the effect of biscuit heat treatment is as follows: "..... the crazing area decreased as the biscuit heat treatment increased from cone 1 to cone 7. With further increase in heat treatment (cone 7 to cone 11) the craze area increased, which checks Hecht's findings ....." The results of the present investigation are concurrent with this in six out of the thirteen results; five curves show a more or less regular increasing tendency to craze from the lower to the higher cones, while on two of the bodies there was perfect fit at the extreme cones and a marked tendency to craze at cone 8. However, as B lies well within Hecht's area and dangerously close to that determined by the preceding class, the general existence of bad crazing at this point is consistent.

At cone 3 there was a general tendency toward crazing of all of Body C trials. As the heat treatment was increased this tendency was overcome until finally, as predicted by Seger's rules, in three instances shivering was made manifest. In the other ten cases the glaze showed perfect fit.

Eight of the sets of Body D trials showed decided *shivering as the heat treatment increased.* This, as also the shivering noted in the Body C curves, was seemingly in direct contradiction to the findings of Professor Purdy.[8] He states: "Shivering occurred with high flint content in the body, the area of shivering *decreasing rapidly as the biscuit heat treatment increased* from cone 5 to cone 11."

The general tendency of Body D to shiver was of course not surprising.

The Effect of Differences in Mineral Constitution of the Ball Clays.

Professor Purdy[9] says: "I know that you cannot substitute one clay for another without expecting a difference, but you cannot prove that the difference lies in the feldspathic material or in the chemical composition. It may lie in the content of other minerals, in the difference in grain or in plasticity and in other things which chemical analysis will not reveal. The question of fineness of grain is very important, and difference in plasticity is quite a factor." On page 199, of the same Transactions, he further says, speaking of Hecht's experiments in which he, Hecht, used varying proportions of kaolin to plastic clay: "Hecht clearly shows the way these boundary lines would be shifted by using different proportions of ball and china clay. Would any one care to claim that these differences in location of the boundary lines are due wholly to difference in mineral make-up of the

[7] Trans. A. C. S., Vol. XIII, p. 167.
[8] Ibid., page 161.
[9] Ibid., page 175.

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clays? If so, I challenge them to bring their proofs. I maintain that these differences in position of the boundary lines between glaze fit and craze areas are due more largely to physical differences in the clays than to chemical differences.

Professor Binns says:[10] "Every clay contains a certain amount of feldspar running from 0.2–0.5 per cent. up to 12 or 15 per cent. If you substitute a clay with practically no feldspar in it for one containing 10 per cent., you are going to increase your feldspar content and decrease your clay content."

It is quite evident from these quoted remarks, that there is a difference in opinion as to cause of differences in effect of the clays.

To throw some light on this mooted point, let us consider the effect produced by the ball clays on glaze fit from the standpoint of their mineral composition. Take the case of H. F. D.'s set of bodies. Body A showed a perfect fit at all cones. This would indicate a ball clay comparatively high in flint either at the expense of clay or feldspar or of both. If at the expense of the feldspar we would expect shivering on Body D at the higher cones, fit on Body C at all cones and craze on Body B. This is exactly the state of affairs portrayed by the curves. The same holds for B.'s set with the exception of his Body C which crazed at cone 3 and shivered at cones 10 and 12.

This glaze had perfect fit on all of H. K.'s Body A, but it also fitted his Body D. We would consider the ball clay in this case high in flint at the expense of the clay, if it were not for the shivering of Body C at cone 10.

M. V. P.'s Body A, all cones, had perfect fit and there was but small evidence of shivering on Body D. This ball clay might be high in flint at the expense of clay. The fact that Body C crazed at the lower cones and fitted at the higher cones seemed to confirm this deduction but in that event there should be a bad case of crazing on Body B, which we did not find.

F. A.'s Body D shivered at all cones. This would indicate high flint in the ball clay at the expense of both clay and feldspar. Why then should Bodies A and C both show evidence of crazing?

R. E. T.'s trials of Body B fitted perfectly; those of Body B crazed at all cones save cone 8; those of Body A crazed at cone 12, as did those of C at cone 3. This might indicate a normal composition, but why the behavior in A and C?

We see then that, although occasionally a consideration of the mineral content of the ball clay seems to throw light on conditions of glaze fit, yet in the majority of cases dependence upon this source leaves us very much in the dark. Whether these wide differences in glaze fit are not affected by the differences in mineral content of the ball clays, or whether we have failed to interpret the results aright, we cannot say. One thing is assured—the

[10] Trans. A. C. S., page 170.

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different ball clays produced widely different results in the glaze fit conditions in bodies that are otherwise identical.

ANALYSIS OF THE MATERIALS.

The above discussion, prepared by Messrs. Thompson and Middleton, was written without any knowledge of the clays. In fact, analyses of clays were not made until about four months

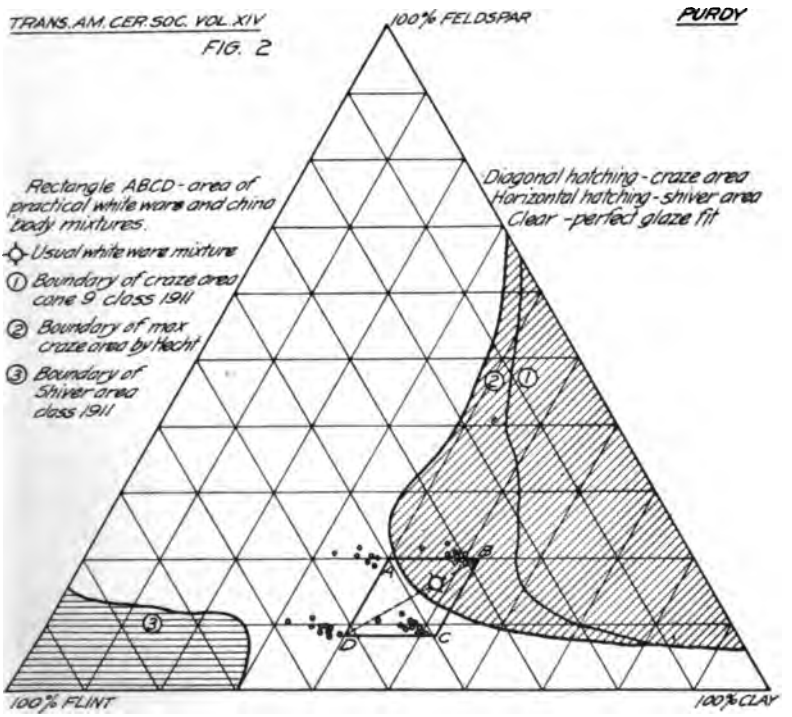

Chart showing changes wrought by **calculated** rational analysis of the materials in the constitution of bodies that had been made up of mixtures of dry materials in proportions represented by points, A, B, C and D.

afterwards and then by a party who knew nothing of the purpose of the analyses.

The following are the analyses of the materials used in these bodies. For analyses of the Ohio silica flint and Canadian feldspar, see page 158, Vol. XIII, Trans. A. C. S.

The clays represented in the tables are: (90) Dillsboro kaolin; (98) Johnson-Porter No. 9; (86) Mandle-Sant No. 9; (51) Mandle-

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TABLE II.—ULTIMATE ANALYSIS.

Lab. No.	SiO_2.	Al_2O_3.	Fe_2O_3.	TiO_2.	CaO.	MgO.	KNaO.	Loss.
90	45.78	36.79	0.50	0.06	0.00	0.00	0.58	16.49
98	51.20	32.10	0.73	1.40	0.13	0.00	0.79	13.75
86	48.53	32.72	0.70	1.30	0.20	0.00	1.50	14.90
51	45.76	38.55	0.60	1.18	tr.	0.20	0.4[13]	11.35
53	61.23	25.05	1.30	1.35	0.10	0.20	1.9[13]	8.35
55	51.81	31.05	1.20	0.75	0.20	0.30	2.6[13]	11.30
65	45.55	33.20	0.70	1.80	0.00	0.00	0.2[13]	18.90
99	52.70	34.17	0.70	1.20	tr.	0.10	0.6[13]	11.65
104	54.70	31.60	0.70	1.00	tr.	0.12	1.4[13]	10.45
112	49.61	34.60	1.20	0.60	tr.	0.07	1.6[13]	12.00
x	47.25	37.23	1.20	1.30	tr.	0.05	0.4[13]	13.05
52[11]	48.54	36.25	0.67	..	0.32	0.32	0.98	12.13
82[12]	47.26	35.85	1.01	..	0.58	0.68	1.19	13.94

TABLE III.—RATIONAL ANALYSIS.

Lab. No.	Determined			Calculated[14]		
	Clay sub.	Feldspar	Quartz	Clay sub.	Feldspar	Quartz
90	93.3	3.5	3.2	95.38	3.57	1.034
98	87.0	3.0	10.0	83.11	4.91	11.98
86	88.7	8.0	3.3	83.89	9.47	6.6
51	99.5	0.4	0.1	97.63	2.37	..
53	71.9	1.8	27.3	60.38	11.67	27.93
55	86.8	0.3	12.9	74.80	16.11	9.04
65	92.0	0.5	7.5	92.17	1.30	6.57
99	85.8	0.8	13.4	85.40	3.57	11.02
104	80.6	0.4	19.0	77.41	8.42	14.16
112	91.1	0.4	8.5	85.35	9.72	4.92
x	97.0	0.3	2.7	95.11	2.42	2.46
52	..	...	..	90.65	5.90	3.44
82	..	...	..	90.59	7.29	2.10

[11] Bleininger and Stull, Trans. A. C. S., Vol. XII, p. 628.

[12] Hope, Trans. A. C. S., Vol. XI, p. 495.

[13] Alkalies not separated. The percentage amounts were calculated as though all were K_2O, hence most of them are too high.

[14] By method and factors given by Pepple, p. 268, Bull. VII, Pt. 1, Wis. Geol. Surv., and recommended by Binns, Trans. A. C. S., Vol. VIII, p. 198, only the KNaO was used in calculating the feldspar content, and this was considered as being all K_2O.

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Sant No. 2; (53) Paducah, Ky. ?; (55) English ball No. 12; (99) Johnson-Porter No. 10; (104) English ball M. M.; (112) English ball H. & G.; (x) Mayfield, Ky.; (52) Mandle-Sant No. 3; (82) Mandle-Sant No. 1; (65) Mandle-Sant No. 5.

In the following tables are the so-called rational compositions of the bodies as calculated from the rational analysis of

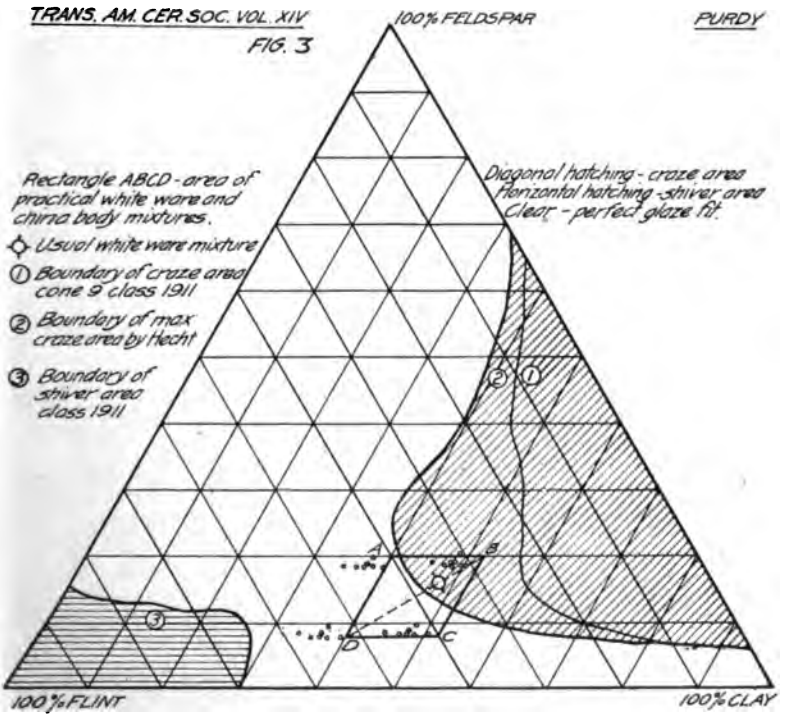

Chart showing changes wrought by determined rational analysis of the materials in the constitution of bodies that had been made up of mixtures of dry materials in proportions represented by points A, B, C and D.

the materials. In these calculations, the flint was taken as pure SiO_2 and the Canadian feldspar calculated from the ultimate analysis as consisting of:

Feldspar	88.2
Clay sub	6.3
Flint	5.5

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TABLE IV.—RATIONAL COMPOSITION OF BODY A, CALCULATED FROM DETERMINED AND COMPUTED RATIONAL COMPOSITION OF THE MATERIALS.

Body A = 20% feldspar, 40% flint, 20% kaolin, 20% ball clay.

Student's initials	Clay No.	Determined			Computed		
		Clay sub.	Feldspar	Quartz	Clay sub.	Feldspar	Quartz
H. F. D.	65	38.32	18.44	43.24	38.77	18.61	42.62
M. V. P.	99	37.08	18.50	44.42	37.42	19.07	43.51
H. K.	86	37.66	19.94	42.40	37.11	20.25	42.63
B.	52	...	...	...	38.47	19.53	42.10
C. P.	98	37.32	18.94	43.74	36.96	19.34	43.71
L. C.	53	34.3	18.70	47.20	32.41	20.69	45.89
L. A. S.	104	36.04	18.42	45.54	35.82	20.04	44.14
G. M.	55	37.28	18.40	44.32	35.30	21.58	43.12
G. F.	82	...	...	...	38.45	19.86	41.73
F. A.	51	39.82	18.42	41.76	39.86	18.83	41.31
R. E. T.	112	38.14	18.42	43.44	37.41	20.3	42.29

TABLE V.—RATIONAL COMPOSITION OF BODY B. CALCULATED FROM DETERMINED AND COMPUTED RATIONAL COMPOSITION OF THE MATERIALS.

Body B = 20% feldspar, 28% flint, 32% kaolin, 20% ball clay.

Student's initials	Clay No.	Determined			Computed		
		Clay sub.	Feldspar	Quartz	Clay sub.	Feldspar	Quartz
H. F. D.	65	49.52	18.86	31.62	50.21	19.04	30.74
M. V. P.	99	46.28	18.92	32.80	48.86	19.5	31.63
H. K.	86	48.86	20.36	30.78	48.56	20.67	30.75
B.	52	...	...	...	49.91	19.96	30.12
C. P.	98	48.52	19.36	32.12	48.40	19.76	31.83
L. C.	53	45.5	19.12	35.08	43.86	21.12	35.02
L. A. S.	104	47.24	18.84	33.92	47.26	20.47	32.26
G. M.	55	48.48	18.82	32.7	46.74	22.00	31.24
G. F.	82	...	...	...	49.90	20.24	29.85
F. A.	51	51.02	18.84	30.14	51.31	19.26	29.43
R. E. T.	112	49.34	18.84	31.82	48.85	20.73	30.41

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TABLE VI.—RATIONAL COMPOSITION OF BODY C, CALCULATED FROM DETERMINED AND COMPUTED RATIONAL COMPOSITION OF THE MATERIALS.

Body C = 8% feldspar, 40% flint, 32% kaolin, 20% ball clay.

Student's initials	Clay No.	Determined			Computed		
		Clay sub.	Feldspar	Quartz	Clay sub.	Feldspar	Quartz
H. F. D.	65	48.76	8.28	42.96	49.46	8.46	42.08
M. V. P.	99	47.52	8.34	44.14	48.11	8.91	42.97
H. K.	86	48.1	9.78	42.12	47.81	10.09	42.09
B.	52	...	..	...	49.16	9.38	41.46
C. P.	98	47.76	8.78	43.46	47.65	9.18	43.17
L. C.	53	44.74	8.54	46.92	43.10	10.53	46.36
L. A. S.	104	46.48	8.26	45.26	46.51	9.88	43.6
G. M.	55	47.72	8.24	44.04	45.99	11.42	42.58
G. F.	82	...	..	...	49.14	9.66	41.19
F. A.	51	50.26	8.26	41.48	50.55	8.67	40.77
R. E. T.	112	48.58	8.26	43.16	48.10	10.14	41.75

TABLE VII.—RATIONAL COMPOSITION OF BODY D, CALCULATED FROM DETERMINED AND COMPUTED RATIONAL COMPOSITION OF THE MATERIALS.

Body D = 8% feldspar, 52% flint, 20% kaolin, 20% ball clay.

Student's initials	Clay No.	Determined			Computed		
		Clay sub.	Feldspar	Quartz	Clay sub.	Feldspar	Quartz
H. F. D.	65	37.56	7.86	54.58	38.01	8.03	53.96
M. V. P.	99	36.32	7.92	55.76	36.66	8.48	54.85
H. K.	86	36.9	9.36	53.74	36.36	9.66	53.97
B.	52	...	..	...	37.71	8.95	53.33
W.	98	36.56	8.36	55.08	36.2	8.75	55.05
L. C.	53	33.54	8.12	58.54	31.66	10.10	58.23
L. A. S.	104	35.28	7.84	56.88	35.06	9.45	55.48
G. M.	55	36.52	7.82	55.66	34.54	10.99	54.45
G. F.	82	...	..	...	37.70	9.23	53.06
F. A.	51	39.06	7.84	53.1	39.11	8.24	52.65
R. E. T.	112	37.38	7.84	54.78	36.65	9.71	53.63

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TABLE VIII.—VARIATION PER 100 PARTS BY WEIGHT IN BODY A DUE TO RATIONAL COMPOSITION OF THE MATERIALS.

	Determined[15]			Computed[15]		
	Clay	Feldspar	Quartz	Clay	Feldspar	Quartz
Actual extreme variation from one another	5.52	1.54	5.44[16]	7.45	2.97	4.59[16]
Actual extreme variation from weights of raw materials.	5.7	1.6	7.2[16]	7.59	1.39	5.89[16]
Percentage mean variation[17] and actual mean variation from weights of raw materials	6.66% 2.66	6.57% 1.31	10.0%[16] 4.0[16]	7.28% 2.91	0.83% 0.17	7.51[16] 3.00

TABLE IX.—VARIATION PER 100 PARTS BY WEIGHT IN BODY B DUE TO RATIONAL COMPOSITION OF THE MATERIALS.

	Determined			Computed		
	Clay	Feldspar	Quartz	Clay	Feldspar	Quartz
Actual extreme variation from one another	5.52	1.54	5.44[16]	7.45	2.96	5.59
Actual extreme variation from weights of raw materials	6.5	1.18	7.58[16]	8.14	2.00[16]	4.26[16]
Percentage mean variation and actual mean variation from weights of raw materials	6.76% 3.51	4.86% 0.97	15.46[16] 4.33[16]	6.67 3.47	1.02[16] 0.20[16]	11.45[16] 3.21[16]

[15] The expressions determined and computed refer to methods of obtaining the rational composition of the materials.

[16] Increases, others are decreases.

[17] Sum of the differences between weights of clay, feldspar or flint originally used and those obtained by analysis, divided by the original weight times the number of cases.

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TABLE X.—VARIATION PER 100 PARTS BY WEIGHT IN BODY C DUE TO RATIONAL COMPOSITION OF THE MATERIALS.

	Determined[18]			Computed[18]		
	Clay	Feldspar	Quartz	Clay	Feldspar	Quartz
Actual extreme variation from one another	5.52	1.54	5.44[19]	7.45	2.96	5.59
Actual extreme variation from weights of raw materials	7.26	1.78[19]	6.92[19]	8.9	3.42	6.36
Percentage mean variation[20] and actual mean variation from weights of raw materials	8.14% / 4.23	6.58%[19] / 0.526[19]	9.32% / 3.73[19]	8.11% / 4.23	20.82%[19] / 1.66[19]	6.37%[19] / 2.55[19]

TABLE XI.—VARIATION PER 100 PARTS BY WEIGHT IN BODY D DUE TO RATIONAL COMPOSITION OF THE MATERIALS.

	Determined			Computed		
	Clay	Feldspar	Quartz	Clay	Feldspar	Quartz
Actual extreme variation from one another	5.52	1.54[19]	5.44[19]	7.45	2.96	5.59
Actual extreme variation from weights of raw materials	6.46	1.36[19]	6.54[19]	8.34	2.99[19]	6.23[19]
Percentage mean variation and actual mean variation from weights of raw materials	8.57% / 3.43	1.33%[19] / 0.106[19]	6.44%[19] / 3.35[19]	9.16% / 3.66	15.44%[19] / 1.24[19]	4.66%[19] / 2.42[19]

[18] The expressions determined and computed refer to methods of obtaining the rational composition of the materials.

[19] Increases; others are decreases.

[20] Sum of the differences between weights of clay, feldspar or flint originally used and those obtained by analysis, divided by the original weight times the number of cases.

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CONCLUSIONS.

(1) Notwithstanding the fact that in these calculations we have included the "rational" composition of the feldspar and kaolin, very little difference from the original weights of the raw materials is obtained. Since the eleven ball clays used in this study were selected at random from the laboratory stock without any knowledge of their composition, we may say that in practical body mixes, the clay substance by rational analysis is but little less than the total clay weighed up originally, that the feldspathic material is only very slightly increased over the weight of the feldspar in Bodies C and D, while it is decreased in Bodies A and B, and that the quartz, by rational analysis of the materials, is in excess of the weight of flint used.

(2) No matter how small or how large these differences may be considered, the balance should be in favor of better glaze fit. This is shown by the facts (1) that in every case the quartz content exceeded the amount of flint weighed up, and (2) that whenever there was an increase in feldspar (Body C and Body D) it was at the expense of the clay substance rather than at the expense of flint. Either of these changes should cause decreased crazing.

(3) According to all data we have on record, there was in no case sufficient increase in quartz content to cause shivering. The maximum actual increase in quartz content in Body D, the one nearest to the shiver area, was only (0.0654×52) or 3.4 parts per 100 batch weight of the body.

(4) Since in the Body D mixtures, the rational analysis of the materials show mean average in feldspar as well as in quartz over the original batch weights of feldspar and flint, respectively, we should expect the changes in composition, wrought by the rational composition of the materials, to be effective toward correction of shivering, and hence in none of the mixtures should we have had an unusual case of shivering.

(5) A comparison of the data and curves of the observed glaze fit, with the data for rational composition of the several bodies and body mixtures, reveals an astonishing discrepancy between what we should have expected (judging from Seger's rules, and their limitations as described last year), and what

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we actually obtained. It is no wonder that the students were discouraged in their attempt to predict the probable variation in mineral content of the bodies.

(6) In no case was the rational composition of the body so different from the original formula as to warrant an expectation of either crazing or shivering in Bodies A, C or D, and the difference in Body B, owing to increase in quartz content, should have been toward better glaze fit.

(7) The data here given plainly show that in the clays usually used in pottery we have factors which influence glaze fit so very much more than does their rational composition as to render the rational analysis data well nigh worthless to the practical clayworker. The only instance in which it could be of service to the clayworker is in the determination of about how much feldspar, etc., a given body contains.

(8) If it were not for the confusion which would result from a large mass of data, we could present proof that variations in translucency, shrinkage, color, warpage, etc., of these same body mixtures did not follow the changes in rational composition.

SUPPLEMENTARY NOTES.

(1) The foregoing conclusions were written before we had the ultimate analysis of the clays, hence they were in no way based on the calculated rational analysis data.

(2) There is no apparent advantage in the calculated over the determined rational analysis and it has the disadvantage of being tedious in making.

(3) From the rational analysis data it appears that in ball clays there is considerable alkali that is not in combination with feldspar while in case of the kaolin (clay 90) all the potash is combined as feldspar. This checks the findings of Seger.[21]

(4) The claim here made against the value of rational analysis is the same as that made by Seger.[22]

(5) That the fine characteristics of porcelain and china are dependent upon the properties of the raw materials as well as

[21] Seger's Collected Writings, pp. 65, 75, 554, 584, 698, 710.
[22] Ibid., p. 689.

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on the percentage mixture of feldspar, clay and flint is well illustrated in the case of Limoges porcelain (see Seger, p. 696). In reporting his attempt to duplicate the fine French porcelain with German materials, Seger says (p. 689): "The question still remains whether bodies thus compounded (on basis of rational analysis) really show the same physical behavior when produced from raw materials of different origin; whether they show the same degree of plasticity and shrinkage on drying and burning. *This question, as a rule*, must be answered in the negative. These properties depend only indirectly upon the chemical composition: they are functions especially of two factors in the body composition, namely, the fineness of grinding of the non-plastic constituents, quartz, feldspar, marble, grog, and the degree of plasticity of the clay substance."

(6) The conclusion that one must draw from the data here obtained and from the experience of Seger is not one whit different than that which I have maintained persistently since writing up the experiments on the floor tile.[23]

(7) This conclusion as to the value of rational analysis is directly opposed to that which has been repeatedly expressed by Binns and others.

(8) The data here given also show the folly of expressing body composition in terms of empirical molecular formula as was recently done by Bleininger and Stull[24] and by others in the earlier volumes of these same transactions.

DISCUSSION.

Professor Grout: I feel called upon to make a statement in answer to the implications that analyses are no good. I am not prepared to discuss analysis in its relation to glaze fit, but I think when Professor Purdy stands on his feet he is inclined to include things besides glaze fit; when he wants to make it cover anything further I want to object. As a mineralogist, I want to call attention to a great many compounds which contain potash in soluble form; we have whole counties in Minnesota where the soil and clay near the surface contain potash in soluble

[23] See Trans. A. C. S., Vol. VII, p. 113.
[24] Ibid., Vol. XII, p. 628.

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form, which would be classed as clay substance in the rational analysis, which would act like orthoclase in pottery, as near as I can tell. The rational analysis, to my mind, is no good for that reason, but when you talk about chemical analysis being useless in the judgment of clay, then, I want to object.

Professor Binns: I think Professor Purdy has given a wrong interpretation of the rational analysis. He has shown that equal amounts of different ball clays behave differently as would, of course, be expected. The point of his contention is that the variations in behavior do not correspond with the variations in composition. If he had made up bodies of the same rational composition using different clays I wonder if he would have found the same discrepancies. If not, his point is not proved. The object of the rational analysis is to enable a potter to maintain the same composition in the body notwithstanding the variations in the separate clays. Furthermore, I recall that Seger insisted upon fine grinding as a condition necessary to a successful use of the rational calculation. If the body mixtures are not of equally fine grain, discrepancies would be found to arise from this cause alone. So far as I know it has not been demonstrated that alkalies in soluble form do not function as fluxes. Some opinions have been advanced but not any evidence. Professor Grout thinks that such alkali would act like the alkali in orthoclase and, therefore, it has no place in the clay substance. I agree with him and this is the main reason for my rejection of the laboratory method or rational analysis. In the calculation method this alkali would be used as an ingredient of feldspar and would thus fall into its proper place.

Mr. Mayer: Speaking of rational analysis and ultimate analysis, I had occasion some time ago to experiment with bodies for vitrified china. I received a car of North Carolina clay which was especially white. The clay was very much superior in color to any English clay I have ever seen, something exceptional. The North Carolina clay I had been getting from the same source was very variable. Ultimate and rational analysis of the clay, which had been made a short time before, showed it to be very similar to a clay I was using, an English

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clay—very extensively used in England by all the china makers, C. D. B. it is called there.

I made up some trials of some bodies; there was no sign of vitrification about them. They looked like semi-porcelain instead of vitrified china. I threw the batch away and tried again; the second time I did not weigh it myself, but it came out the same way. I still thought there was a mistake, but when the third trial came out the same as the others, I decided to test the clay in the elutriating machine. We have a common standard in our flint—we cannot use any that does not show between 12,000 and 13,000, and this clay showed an elutriation test between 11,000 and 12,000—the English clay I was using showed about 16,000. I am giving these figures from memory, but I am correct in saying the North Carolina was coarser in grain than our flint. By analysis, the English and North Carolina clays were the same, but the coarse grain of the North Carolina clay made it unfit for use in a vitrified body at the temperature at which we were firing.

Mr. Watts: Regarding the size of grain of North Carolina kaolin to which Mr. Mayer has referred, I would say that notwithstanding its complete kaolinization as indicated by chemical analysis, it is certainly coarser than the English china clay and lower in plasticity. In my investigation of these clays, I find that while the kaolins of North Carolina as marketed will practically all pass a 200-mesh sieve, the proportion of extremely fine material, as indicated by an elutriation test, is very low, as compared with English china clays. The record of size of clay grains is only of value when it includes the proportion which are approximately one thousandth inch diameter, one five-thousandth inch diameter, one ten-thousandth inch diameter, and even smaller. Such a gradation is effected by an elutriation separation and the absence of these very fine grains in the North Carolina kaolins is doubtless the cause of the lack of vitrification noted by Mr. Mayer.

NOTE PREPARED AFTER READING THE ABOVE DISCUSSION.

Mr. Purdy: Neither Mr. Grout nor any other one who has expressed himself on the value of chemical analysis has been

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able to show ability or even profess ability to prophesy from chemical analysis concerning the working, drying or burning behavior of a clay. A great deal of generalities have been stated concerning the usefulness of chemical analysis, in which special cases have been used as illustration. To the thinking man, however, citation of special cases will not prove generalities, and generalities concerning the value of chemical analysis should not have been taken as proving that the analysis of clay has the value which writers in State Geological Survey reports would have us believe.

Now, my position on the question of the value of chemical analysis is exactly that taken by Seger.[25] I know that there are many instances where a chemical determination of a substance or substances in clays explained some peculiar phenomenon that had been observed. I know with equal certainty, however, that the peculiar phenomenon could not have been predicted with confidence from the chemical analysis. I advocate and practice the making of special analysis but I can see no value in an ultimate or rational analysis as means of predicting the useful properties of a clay.

A careful study of Seger's writings will reveal also that my estimate of the value of the rational analysis is not much, if any, different from that which he states. I do not believe, and I do not say, that the rational analysis is wholly without value. In fact, I have more faith in what Dr. Seger says it will do than most *students* of ceramics. The technical value of rational analysis is nicely illustrated in Seger's writings especially in his treatises on "Limoges Porcelain Materials," (p. 695). "The Copenhagen Bisc Ware" (p. 707), and "Composition of Some Foreign Hard Porcelain Bodies" (p. 678).

As I said in my paper, if feldspar is present in the clay, the determined rational analysis will find it with accuracy. In our work on ball clays, pure unaltered orthoclase feldspar was added to those samples in which no feldspar had been detected, and, by analysis, we recovered the feldspar very accurately quantitatively. The same may be said of the quartz determination.

[25] See Seger's "Collected Writings" (Amer. Cer. Soc., Edition), pp. 8–11 for example.

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There is absolutely no question but that the determined rational analysis will accurately separate kaolinite, feldspar and quartz quantitatively. It is for this reason that the rational analysis is of great value in such studies as are described by Seger and just referred to by me.

Now, I have promised that at a future date I will discuss the claim which I have made,[26] to wit, "that the assumptions on which both the so-called rational analyses are based, are not in agreement with facts. I will not go into this discussion at the present time except to call attention to two facts.

First, Seger[27] recognized many of the factors which make unsound the premises on which the rational analysis is based.

Second, as an illustration of the fact that clays may contain minerals other than kaolinite, feldspar and quartz, I will cite a mineral mixture which had been sent into this office as kaolin. Fifteen per cent. of this material went into solution when digested with sulphuric acid and caustic soda, indicating, of course, the presence of 15 per cent. clay substance. The ultimate analysis and calculated rational analysis of this material were as follows:

Ultimate analysis.		Calculated rational analysis.	
SiO_2	70.00	Clay substance	63.24
Al_2O_3	25.55	Feldspar	3.55
Fe_2O_3	tr.	Quartz	38.50
TiO_2	0.22		
CaO	tr.		
MgO	tr.		
K_2O	0.60		
Vol.	3.93		

A close study of these figures would show that neither the determined nor the calculated rational analysis gave the correct constitution of this mineral mixture. The determined rational was quite evidently wrong, for although the clay contained only 0.60 per cent. K_2O, nearly all of the Al_2O_3 was in the insoluble portion. This Al_2O_3 in the insoluble portion was at first taken as being indicative of a high feldspar content which, of course, with this low K_2O was a ridiculous supposition.

[26] Trans. A. C. S., Vol. XIII, p. 200.

[27] Seger's "Collected Writings," pp. 57, 63, 65, 74, 76, 513, 682.

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The data on the calculated rational was obviously as ridiculous as the determined for there could not be so large a discrepancy between the determined and the calculated as is indicated by the figures 15 and 63.

The secret of the difficulty was that we were dealing here with a mixture of 15 per cent. clay substance, and 85 per cent. pyrophyllite (Al_2O_3 4 SiO_2 H_2O) which is practically insoluble in H_2SO_4. This shows that if the clay should contain minerals other than kaolinite, feldspar and quartz, as many do, the rational analysis can not determine the nature of this mineral mix.

While I do not doubt in the least that the sulphuric acid method of rational analysis will accurately differentiate between kaolinite, feldspar and quartz without regard to the physical conditions of these minerals, I maintain that these exact quantitative data, even when the clay is wholly kaolinite, feldspar and quartz, are not sufficient to determine the effect of the clay on glaze fit. Seger (p. 576), Hecht, and others have shown that the more plastic the clay, the better will be the glaze fit. Seger (p. 577 and p. 76) has shown also that the size of the quartz grain is a very important factor in glaze fit. No one, I think, will claim that these physical factors can be determined by either of the methods of rational analysis. It is for these and similar reasons that I reaffirm all that I said in Volume XIII[28] on this subject.

That we may have a record of the appreciation on the part of others of differences wrought by physical factors, I cite the following. In doing this I make no claim of agreeing with all the conclusions indicated in the abstracts. I make note of some of the places wherein I differ with the writers.

FACTORS THAT EFFECT DIFFERENCES IN QUALITY OF WARES.

That the fine characteristics of porcelain and china are dependent upon the properties of the raw materials as well as on the percentage mixture of feldspar, clay, and flint is well illustrated in the case of Limoges porcelain (Seger, p. 696), and as to duplicating the fine French porcelain with German materials, Seger has already been quoted.

[28] Pp. 169–176, 183–209.

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The effects of fineness of grain of feldspar and flint are shown in the following references:

(1) Binns, Trans. A. C. S., Vol. V, p. 281. In this article, Binns demonstrates that finer grinding results in more vitreous and whiter biscuit.

(2) Mayer, Trans. A. C. S., Vol. III, p. 36; Vol. IV, p. 28. In the first of these articles, Mayer emphasizes the fact that coarse material gives trouble by settling, not only in the operation of the blunger and slip tank but in the making variable the body composition.

In the second article, Mayer demonstrates that the English wet ground flint is not only finer, but produces more vitreous biscuit.

(3) Burt, Trans. A. C. S., Vol. III, p. 17. Burt experimented with five flints, two American rock, one French calcined, and two sand. He claimed a difference in the behavior of each but failed to trace the difference to any single condition of the flint.

(4) Orton, Trans. A. C. S., Vol. II, p. 118; Vol. III, p. 204. Orton experimented with mixtures of Mayfield ball clay and sands, in each mixture the sands being of different fineness. He found that after the sand was ground to a certain degree of fineness, it caused the briquette to crack in drying, thus decreasing very materially its tensile strength. In his second article he demonstrated that the briquette containing the finest sands could be dried safely if the drying was restrained.

(5) Zimmer, Trans. A. C. S., Vol. II, p. 123, cites actual factory experience in which he found that ware cracked in drying, owing to the flint being too fine.

(6) Galpin, Trans. A. C. S., Vol. XII, p. 548. Galpin studied the effect of varying sizes and percentages of quartz grains upon porosity and shrinkage of kaolin. Galpin concludes that "the coarser the grains in the mixtures, the greater the reduction of shrinkage and the less the reduction of porosity; the less water required in tempering, the less tendency to warp or crack in burning; the fewer the gas vesicles formed in the ware."

(7) Krehbiel, Trans. A. C. S., Vol. VI, p. 173. Krehbiel claims that "it is better to grind flint than feldspar."

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(8) Keele, Trans. A. C. S., Vol. XIII, p. 731. Keele says: "The action then that goes on in the heated body appears to be the gradual absorption of kaolin by the molten feldspar. The fine grinding evidently facilitates and accelerates the absorbing capacity of the feldspar, as it exposes a greater surface for reaction with the clay particles.

It follows then that the finely ground feldspar requires less time to mature a pottery body, that such a body does not approach so near to fusion (*i. e.*, to losing shape) and that the tendency to bending and warping is much reduced." (Compare this statement with that of Galpin and also with that of Ashley.)

(9) Trans. English Ceramic Society.

Volume II. "The Effect of Varying Fineness of Particles of Non-plastic Materials in Pottery Bodies," by A. Heath.

Volume II. "Comparison of Physical Properties of Cylinder and Pan-ground Flint," by W. Jackson.

(10) Ashley, Trans. A. C. S., Vol. XIII, p. 434 and p. 437.

"A uniformity of grinding is very essential since, other things being equal, a change to finer quartz tends toward cracking of the ware and increased biscuit loss; while a change to coarser quartz tends toward crazing, reduced biscuit loss, and straighter ware."

"The more finely ground a feldspar is, the more uniform will be its distribution through the body, and the larger will be the area upon which it first exerts its cementing action. If in coarse grains, it will have to flow to fill the various pores, and reach the grains of quartz and clay that it is to cement together; but if fine ground, it will merely have to soften in position. *It follows then that the fine ground feldspar requires less time to mature a body, that the body thus does not approach so near to fusion, its particles are less disturbed, and the tendency to bending and warping is much reduced.*"

See discussion by Purdy on this point, p. 453, Vol. XII.

On the comparative effect of kaolin and ball clay, aside from their effect on the working properties in the plastic condition and on glaze fit, we have very little evidence in print. The following are some of the data on this point:

(1) Mellor, Trans. Eng. Cer. Soc., Vol. VI, p. 75. Mellor

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expresses the belief that ball clay is not so readily attacked as china clay notwithstanding the fact that when heated alone the ball clay begins to fuse at the same temperature (1100° C.) at which the china clay particles begin to lose their identity in the feldspar magma.

(2) Watts, Trans. A. C. S., Vol. X, p. 199: "In the proportion of 70 per cent. clay and 30 per cent. feldspar, and fired at cone 12 in a 40-hour burn, I find that the ball clays display notably less solubility in the fused feldspar than do the china clays, although the ball clay porcelain displays by far the finer texture."

(3) Bleininger and Stull, Trans. A. C. S., Vol. XII, p. 628, in research entitled "A Study of the Vitrification Range and Dielectric Behavior of Some Porcelains," give evidence which apparently is not in keeping with the observations by Mellor and Watts. On pp. 653 and 656, they exhibit "apparent porosity curves" which show that the Tennessee ball clay mixtures vitrify earlier and more rapidly than the Georgia and North Carolina kaolins and when the clay content is 60 per cent., they vitrify earlier and more rapidly than the English china clay mixtures."

These same facts are shown in another way in the curves on pp. 658, 659, 661 and 662 of the same article.

These investigators show on pp. 667, 668 and 669 that the ball clay mixtures have a larger range of composition over which maximum dielectric strength is obtained, which fact shows that the ball clay mixtures burned to a denser structure. This is also shown in curve on p. 310, Trans. A. C. S., Vol. X.

These results by Bleininger and Stull do not necessarily refute the statements by Mellor and Watts regarding the comparative readiness with which ball clay and kaolin go into solution for neither total decrease nor the rate of decrease in porosity is due wholly to fusion. In fact, on the contrary, more rapid rate and more complete fusion may result in *increased* porosity through formation of bleb structure.

(4) Bleininger and Boys (Trans. A. C. S., Vol. XIII, p. 387) state that "in discussing the vitrification of clay, we are somewhat too prone to ascribe the closing up of the pore system entirely to the action of fluxes which cause incipient softening and the

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resulting lack of molecular cohesion due to the decreased viscosity. Part of the contraction is undoubtedly caused by the shrinkage of the colloidal portion of clays, since, indeed, such condensation is typical of amorphous substances in distinction from crystalline materials."

If by colloids, Bleininger and Boys refer to extremely fine particles, their statement is entirely correct as to observed facts but not necessarily so as to the explanation which they give by way of analogy. That they are not wholly correct in assuming that condensation which results in decreased porosity is due to shrinkage of colloids, is proven by experiments by Pense (Trans. A. C. S., Vol. XII, p. 53) in which he determined the effect of colloidal silica on clays. He reports that "The results show decreased vitrification with increased colloidal silica acting much the same as would a similar increase in flint."

(5) Chemically, kaolin and ball clays are not unlike except in the composition of the clay substance; *i. e.*, the portion soluble in H_2SO_4. The clay substance of ball clays is higher in alkalies and the clay substance of kaolin approximates the analysis of kaolinite. See Seger, pp. 65, 75, 554, 584, 698 and 710.

Now, returning to Professor Binns' discussion, I note that Professor Binns' recollection is that Seger insisted upon fine grinding, as a condition necessary to a successful use of the rational calculation. Taking it that Binns meant rational analysis rather than calculation, I beg to suggest that his memory fails him. Seger describes his method on pp. 50–62 and discusses its value on the other pages I have cited. In none of these does he mention fine grinding as being necessary to this determination.

If by this reference to fine grinding Professor Binns is granting that size of grain is a factor in control of the effect of clay in pottery bodies, then he is beginning to admit that there is at least one important factor concerning clays which rational analysis can not give information.

No one questions but that alkalies in soluble form "function as fluxes." That is not the issue. The issue is: Does the alkali in soluble form have the same effect as the alkali in feldspar? By this, of course, is meant: Can we assign to the soluble alkali, Al_2O_3 and SiO_2 in the proportions found in feldspars, and consider

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that these will function the same as feldspar? This, I have shown,[29] by several examples, can not be the case and I have challenged Binns to disprove my contention. He has made no attempt to do this but repeats, in the above discussion, his opinion. I want evidence, not opinion. I commend to him the testimony of Professor Bleininger as recorded on p. 30. Tech. Papers of Bureau of Standards, No. 7, in which he says: "Thus, owing to the high viscosity of feldspar, its mechanical softening effect is not as marked as it would be if an equivalent amount of free alkali were added."

[29] Trans. A. C. S., Vol. XIII, pp. 194–195.

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NOTE ON THE FUEL CONSUMPTION OF SOME WHITE-WARE KILNS.

By THOS. GRAY, E. Boston, Mass.

A description is given by Mr. E. Montgomery in the Transactions of the American Ceramic Society, Volume XIII, page 311, of a very economic kiln, downdraft, with an inside stack. Below is given in tabular form a description of four kilns in use at the plant of the New England Pottery Co. For the purpose of comparison, there is also given a description of Montgomery's kiln.

In giving the number of bungs, Mr. Montgomery does not mention the size of his saggers. In case of the New England Pottery Co.'s kilns, the number of saggers mentioned include common, oval, coffin, single and double plate, cuspidors, etc.

As Mr. Montgomery invites comparison, I would call attention to my experience in regard to the economy of kilns. Kilns No. 1 and No. 2 were built in 1856 by Nutt, of Trenton; No. 4 about 1867; and No. 3 in 1903, by Louis Nutt, of Trenton. My personal knowledge goes back forty years. In that time No. 1 and No. 2 have been in constant use except for seven months, and No. 4 has been idle for about ten years. Kiln No. 3 is economic in firing, but has been an unlucky kiln, and we do not use it more often than necessity calls for. During 1897, all three of the stacks from the crown up and the crown were rebuilt. No. 1 and No. 2 were also rebuilt about the doors. The inside walls just above the bags have been repaired where they burned out and bottoms and fire boxes of course had to be rebuilt. However, the walls of the kilns have been up to two years ago as good as when first built. No. 4 is not in as good condition as No. 1 and No. 2; neither is No. 3, although it has been standing only eight years. All the kilns are very lightly banded.

Some years ago, I understood that a $15^1/_2'$ kiln was considered the ideal size. I think our experience would indicate that there was some truth in the theory.

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UPDRAFT KILNS IN USE BY THE NEW ENGLAND POTTERY CO., EAST BOSTON, MASS.

Number of kiln	Diameter	Height to ring of crown	Height to center of crown	Number of fire boxes	Capacity		Tons bituminous coal used in firing[1]	Firing temperatures Cones	Use
					Bungs	Saggars			
1.....	15½′	15½′	18′	10	75–80	1800	8–9	8	Gloss
2.....	15½′	15½′	18′	10	75–80	1800	8–9	8	Gloss
3.....	16½′	17′	20½′	10	90–97	2400	9½	8	Gloss and biscuit
4.....	17½′	17′	19½′	11	103–108	..	11–12	9	Biscuit
MR. MONTGOMERY'S KILN AS DESCRIBED.[2]									
	18′	13′	15½	9	125	3750	9	11	

[1] 2,000 lbs. to the ton.

[2] With an inside stack 3′ 9″ in diameter (outside measurement).

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DISCUSSION.

Prof. Orton: I want to say I derived benefit from this paper. It shows the necessity of getting down with the kiln, or the dryer, or the tool that you may be using and making an extensive study of what its performance is, and then remedying whatever defects you may find. The paper as an illustration of the mode of study that will bring results is, in my opinion, excellent.

NOTES PREPARED AFTER READING THE PAPER.

Mr. E. T. Montgomery: I am glad that Mr. Gray has given us this efficiency record for updraft potter's kilns and has tabulated the data for his kilns and for the downdraft kiln which I described last year, so that they may be easily compared.

To make the comparison complete, I will add that for the kiln I described, the saggers were 14" round and square saggers of varying heights but averaging 30 to the bung or 3750 to the kiln. Mr. Gray does not give the length of burn in hours necessary to reach the designated cones, but I believe that the time was about the same in both cases. I also wish to add that during the time that the data was taken, which has been given in these two papers, the downdraft kilns which I have described and the updraft kilns which Mr. Gray describes, were fired by brothers, both excellent firemen of many years' experience and men who got the full value out of every shovelful of coal used. For this reason this comparison of the two types of kiln is especially valuable.

Considering now the data as given, we see that while we cannot figure accurately the sagger capacity of the two types of kiln in cubic inches of placing space, we can compare them very closely by figuring in cubic feet the effective kiln space in both cases. This we find to be about equal for both types of kiln as described. We see then that the downdraft kiln fired about the same quantity of ware three cones higher, using the same amount of coal, and in the same length of time.

Mr. Gray: The time of burning in our kilns, which Mr. Montgomery asks for, was about 46 hours for the biscuit and $22^1/_2$ hours for the glost kilns. Mr. Montgomery uses one ton

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of coal to each fire box, while my figures give eight tons in ten fire boxes for the glost kilns and a little less than a ton in the biscuit.

The great economy I claim is the small expense for repairs my kilns show in the over 50 years they (the No. 1 and No. 2) have been in constant use; and they are good for several years to come.

Another economic feature is the good results we get from No. 1 and No. 2, which we do not obtain from No. 3 with as much certainty. I am satisfied with my updraft kilns.

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NOTE ON LOAD TESTS MADE ON MAGNESITE, CHROME, AND SILICA BRICK.[1]

By G. H. Brown.

LOAD TEST ON A MAGNESITE BRICK.

Although magnesite brick are designed mainly to withstand the corrosive action of molten slags and metals such as are encountered in the basic open hearth furnace, cases have arisen where brick of this type have been used mainly on account of the fact that their refractoriness is superior to that of clay brick. It was, therefore, thought that a load test similar to that applied to clay fire brick and described elsewhere would be of interest.

One from a lot of magnesite brick purchased on the market was placed in the testing furnace on end and a load of 50 pounds per square inch applied. The rate of temperature increase to 1350° C. was the same as that used in testing clay fire brick,[2] the temperature being held, however, at 1350° for one half hour and then increased at the same rate. At 1550° C. the lever of the furnace dropped suddenly without warning and without previous visible contraction of the brick as far as could be observed from the spirit level in place on the beam.

Upon examination the brick was found to have sheared diagonally into two parts, the break being similar to that we would expect on testing cold in a compression machine. There was no bending of the brick in evidence. The only appearance of softening was at the edge of the brick which struck the bearing block of the furnace when failure took place. This edge had been flattened and bore the imprint of the depression of the bearing block.

The failure was very dissimilar to those secured on fire brick made from clay.

Whether the failure could be accounted for by the softening of the bonding material or whether it was due to a molecular change which weakened the structure, we have not decided. The suddenness of the failure and the character of the fracture inclines towards the latter theory, however.

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[1] By permission of the Director of the Bureau of Standards.

[2] Vols. XII and XIII, Trans. A. C. S.

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The published analysis of the material from which these bricks are manufactured is as follows:

SiO_2	2.84
Al_2O_3	0.929
Fe_2O_3	8.571
CaO	1.120
MgO	85.32
CO_2	0.50

LOAD TEST ON A CHROME BRICK.

One from a lot of chrome or so-called neutral brick was subjected to a test similar to that given the magnesite brick. The furnace was held at 1350° C. for one-half hour and the temperature gradually increased from that point. The behavior of the brick during the test was very similar to that of the magnesite brick, failure, however, taking place suddenly at 1450° C. There was no previous indication of contraction. Upon examination the brick was found to have sheared diagonally into two parts. There was no bending or evidence of softening.

The[3] published analysis of chromite or chrome ore, from which similar brick are manufactured, shows the following:

Cr_2O_3	38.0 -40%
Al_2O_3	24.5 -40%
Fe_2O_3	17.5 -40%
SiO_2	3.25-40%
MgO	15.0 -40%

As in the case of the magnesite brick the failure was unlike that secured on clay fire brick and has been unaccounted for.

In making the preliminary load tests on fire brick it was first thought that the transverse test would be most suitable. Samples of fire brick were supported at the ends and a load applied at the center of the flat side of the brick. At temperatures above 900° C. and below 1150° C. the brick would suddenly fail without appreciable deformation or previous warning. The failures were thought to be due to the volume changes in the brick. In testing fire clay brick more or less expansion is noted between the above temperatures, although in testing on end failure has never resulted from this cause.

Perhaps pronounced volume changes occurring in the mag-

[3] "A Study of the Open Hearth," H. W. R. Co.

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nesite and chrome bricks at the higher temperatures would account for their failure.

LOAD TESTS ON SILICA BRICK.

Upon subjecting a sample of silica brick to a load of 50 pounds per square inch on end and holding at a temperature of 1350° C. for one hour no contraction resulted. After cooling the furnace down rapidly, however, the silica brick was found to be badly cracked. Under the same cooling treatment cracking was never observed in any clay brick tested. In another test on silica brick it was subjected to a temperature of 1470° C. under a load and was not affected.

The silica brick tested were of the variety manufactured from crushed quartzite, using lime as a binder.

Silica brick in which clay has been used as a binder show a small deflection under a load at 1350° C.

DISCUSSION.

NOTE PREPARED AFTER READING THE PAPER.

Mr. Kerr: I am very much interested in the notes prepared by Mr. Brown on the results of his tests with these special refractory bricks. From my own experience with refractory wares it seems to me that the analysis, as made by Mr. Brown, is in agreement with all information which is now available upon this subject.

Where the failure is of the character described by Mr. Brown, in referring to the magnesite and chrome bricks, it does not seem quite reasonable to attribute the failure to the failing of the bonding material. Such failures it would seem are more apt to result from some molecular rearrangement causing a change in specific volume.

It would be most interesting to compare the absolute specific gravity of the materials in the original bricks with the specific gravity of the materials after the test, the samples being obtained by quenching in water to prevent reversion to the original forms. In making load tests of this sort it is most interesting to note changes in porosity and specific gravity which occur at the time of failure. I have, however, no data to offer which would throw any light upon the tests which Mr. Brown reports.

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NOTE ON THE SPECIFIC HEAT OF CLAY.

By J. M. KNOTE, Pittsburgh, Pa.

INTRODUCTORY.

For various reasons the subject of the specific heat of clay has not received much attention, but it seems of interest to note the effect of increasing temperature on this property.

Landolt-Börnstein's "Physikalisch Chemische Tabellen" gives the specific heat of kaolin as 0.2243 at 22° C. to 98° C. Bleininger and Moore, Transactions of the American Ceramic Society, Vol. X, use the value 0.2 but state that they had determined it as 0.235 between 440° C. and 1000° C.

The points taken up in this paper are the specific heat of a raw clay determined and calculated, the effect of dehydration on the specific heat, the effect of the change which takes place at 950° C. producing such a pronounced change in the specific gravity of a dehydrated clay.

Theory.—By specific heat is meant the capacity of a substance to absorb heat, compared with that of water. The fundamental principle which enables one to understand the value and changes in the specific heat of a substance is expressed by the law of Dulong and Petit that the capacity of atoms for heat is approximately the same for all solid elements. Kopp showed that frequently the molecular heat of a solid compound is equal to the sum of the atomic heats of its component atoms. Thus the specific heat of a substance depends on its chemical composition; and so long as that remains unchanged, the specific heat is the same except for changes produced by changes in temperature. It has been determined that the specific heat of the solid elements increases about 0.04 per cent. for each degree Centigrade increase in the temperature; and the mean specific heat to zero half that fast, although according to some experimenters the silicates increase more rapidly up to a low red heat than they do beyond that temperature.

EXPERIMENTAL.

Method.—An Emerson calorimeter which had been standardized repeatedly was employed. Weighed samples of clay in assay crucibles were put into an air oven, which was then

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held at a constant temperature for several hours. When the calorimeter was ready the oven door was opened and a crucible covered with a clay scorifier which had been in the oven beside the crucible. The crucible was then picked up in the gloved hands and the contents quickly dumped into the calorimeter. The whole operation required only a few seconds.

Clay Used.—As has been pointed out the specific heat of a clay depends on its chemical composition, and but few clays would return exactly the same value. For this reason our results, though carefully determined, apply to this clay only.

A flint clay from Olive Hill, Kentucky, was selected for this work. Its composition was as follows:

Silica	53.30%
Oxide of aluminum	30.88
Oxide of iron	0.71
Lime	0.50
Magnesia	0.08
Titanic acid	2.21
Alkalies	0.12
Water	12.24
	100.04

Determinations.—A couple of pounds of the material was ground to pass an eight mesh screen and remain on a sixteen mesh. A portion of this was kept unburned, part was burned to 650° C. in sixteen hours and the rest to 1050° C. in twenty-four hours. All results were obtained from 22° C. to 150° C. so as to get a comparison of materials and eliminate the effect of temperature.

Raw Clay.—An average of five closely agreeing determinations gave a result of 0.237. Approximately the same value will be arrived at by calculation, using the values usually given for silica, oxide of aluminum, hydrogen gas and oxygen gas.

Clay Burned to 650° C.—A series of five determinations averaged 0.204. This also agrees closely with the calculated result. Loss of water accounts for the decrease in specific heat.

Clay Burned to 1050° C.—Five determinations averaged 0.200. That no change in specific heat accompanies the change in specific gravity at 950° C. is due to the fact that the chemical

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composition has not changed, *i. e.*, the same elements are present in the same proportions.

CONCLUSIONS.

The specific heat of a clay is lowered by dehydration, as one would expect. The value for clay burned to 1050° C. is but a trifle lower than that of the 650° material. This is probably due to the fact that the last traces of water have not been expelled at 650°.

DISCUSSION.

NOTES WRITTEN AFTER READING THE ABOVE PAPER.

Professor Staley: It must be borne in mind that the specific heat of substances of the same chemical composition, especially silicates, does not depend wholly on chemical composition and temperature, but depends also on whether the substance is a crystal or glass, whether it is in one crystalline form or another

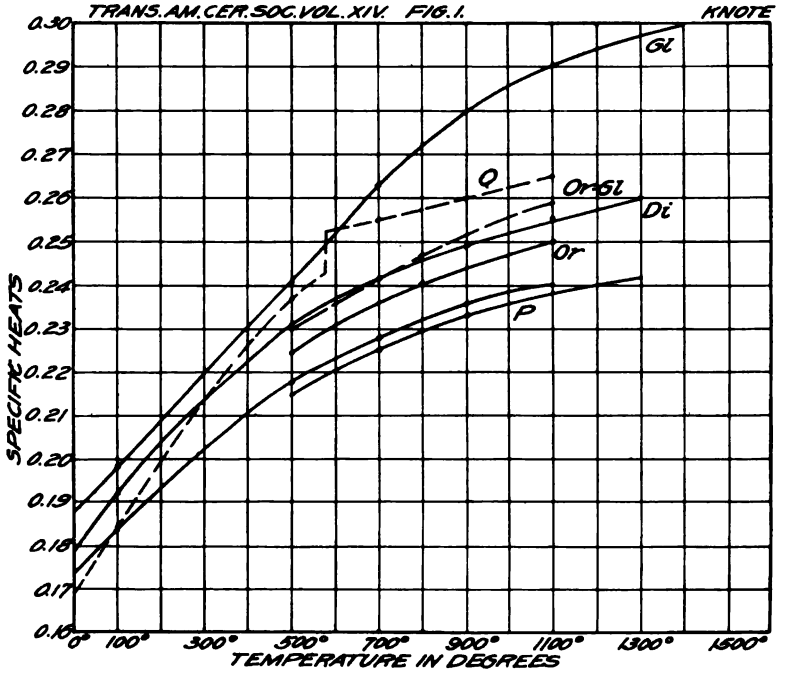

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TABLE 1.—MEAN SPECIFIC HEATS FROM ZERO, OF PLATINUM, PSEUDO-WOLLASTONITE, WOLLASTONITE, ORTHOCLASE, DIOPSIDE, QUARTZ, ORTHOCLASE GLASS, AND A SOFT TUBING GLASS.

Upper Temperature	Pt.	P-Woll.	Woll.	Or.	Di.	Qu.	Or. glass	Soft glass
100°	...	..	1833	..	1919	1840	..	1977
	...	..	1833	..	1905	1851	..	1974
	...	..	..	..	1920	..	..	..
500	03348	2159	(2180)	2248	2310	2372	2291	24000
	03355	2169	2169	2246	2308	2368	2304	24077
	...	..	2168	..	..	..	..	2413[2]
	...	..	..	..	..	..	..	2410[2]
700	03423	..	2286	..	2420	(2547)[1]	..	2646
	03428	..	2289	..	2422	2559[1]	..	2639
	...	..	..	..	..	2556[1]	..	..
800	...	..	..	2401	..	..	2465	..
	...	..	..	2402	..	..	2473	..
900	03515	..	2354	..	2499	2597[1]	..	2791
	03514	..	2355	..	2488	2594[1]	..	2796
	...	..	..	..	2483	..	..	..
1100	03573	2380	(2423)	..	..	..	..	..
	03578	2380	2404	2505	2562	2643[1]	2588	2907
	...	2375	2404	2513	2564	2646[1]	2591	2909
	...	..	2403	..	..	..	..	..
1300	03640	2422	..	..	(2613)	..	..	2945
	03647	2416	..	..	2596	..	..	2949
	...	..	..	..	2601	..	..	2972
	...	..	..	..	..	..	..	(2996)
1500	03675	..	..	..	..	..	..	2999
	03682	..	..	..	..	..	..	2998
	...	..	..	..	..	..	..	3024

[1] Affected by the inversion at 575°. [2] Heated by lead bath.

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and, in general, on the internal molecular arrangement of its particles. For instance, the mean specific heat of quartz crystals at temperatures between 12° C. and 100° C. is 0.185, while the mean specific heat of amorphous silica[3] (opal) at the same temperature interval is 0.2375. In Table I[4] and Fig. 1,[4] are several other examples.

Mr. Knote: To make my statements concerning specific heat complete, I should have included the factors Professor Staley cites, but they are very much less important than the others. This is very evident from my results, and it is impossible to say whether the slight difference between the 650° C. and the 1050° C. samples is due to complete loss of water at the higher temperature or to the factors in question. Certainly great physical changes do not produce much of a result on this property.

The great difference Professor Staley cites between quartz and opal is probably due to the fact that the latter always contains considerable water which has a great effect on the specific heat.

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[3] J. Joly, Proc. Roy. Soc., XLI, p. 250.

[4] Taken from article by W. P. White on "Specific Heats of Silicates and Platinum," Amer. Jour. Science, Vol. XXVIII, p. 334.

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SETTLING AND FILTERING OF FIRE CLAYS.

By GEORGE E. THOMAS, St. Louis, Mo.

The fire clay mined by the Highlands Fire Clay Co., when exposed to weathering, seems to be greatly benefited by exposure for a long period of time; and it has been our experience that there is a certain standard of time required to obtain certain results, after which time no further benefit is noticeable in the process of settling and filtering.

The clay as mined is a hard rock-like mass and weathering reduces it to an easily crumbled powder. Nevertheless, a mere disintegration, such as occurs at the surface of the weathering piles, is not sufficient.

The clay freshly mined and exposed to weathering for a period of two years and over appears to go through a change that puts it into such a state that, when mixed with water to a clay slip, settling of the clay begins as soon as the slip is placed in the settling tank, the water separating on top being as clear as if filtered. It has been noted that in a six foot depth of slip a separation of clear water of twenty-four to thirty-six inches has taken place in several hours, leaving the clay a thick heavy slip below; and as this clear water is drawn off, the clay continues to settle until it is very heavy and contains very little water.

Whereas in the same clay when exposed to weathering for a shorter length of time (one-half to one and one-half years) and put through the same process as stated above, a separation of only one-half inch to six inches of water takes place in the settling tubs, and this water does not separate from the clay clear, it being of a cloudy, milky appearance. No further change takes place whatever whether allowed to settle one day or fourteen days. In the filtering through filter presses water will not separate from the clay easily; and it requires double the time required for the older clay to press out the surplus water, even under the same pressure, and no difference is observed if higher pressure is used. The cakes will not filter solid; they form a thin layer of clay next to the filter cloth and hold a soft, mushy mass of clay in the center, which remains in this state regardless of pressure or time. Also there remains upon the cloth a slimy, sticky clay

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substance which seems to coat the cloth and make it waterproof, while with the older clay the cloth is left clear and dry when the solid cake of clay is removed.

In the weathering, let it be understood, the clay in both cases is tested under exactly the same conditions, the only difference being the length of time of exposure to the weather.

It has been found with this clay that after the change has taken place, as in the two-year old clay, no appreciable change or benefit was experienced by aging the clay up to five years, the filtration and settling of the two-year and five-year clays being alike.

As far as we can learn, there is nothing in the chemical analyses of the two clays which would explain or cause the difference in their working.

Our aim is to learn if possible what change takes place, and the cause, to make such a vast difference in the workings of the two clays and whether or not the same results cannot be obtained by other means than the weathering process.

DISCUSSION.

NOTES PREPARED AFTER READING THE PAPER.

Mr. Watts: This peculiar behavior may be due to incomplete solubility of the alkali in the fire clay. In the study of primary kaolins, I have found cases where the kaolin as mined dissolved with difficulty and when made up into a thin slip would settle out but leave the water milky, and this would not settle for days. Kaolin from the same workings which has laid on the dump or been otherwise exposed to weathering action settles in a short time leaving a clear liquid. In handling such kaolins directly from the mines it is customary to use a solution of alum as an electrolyte to flocculate the kaolin. This is introduced in lump form in the trough through which the kaolin slip must pass to the cistern. The amount used is very small and the kaolin settles in a few hours to a dense mass from which the excess water may be drawn off without difficulty. Other electrolytes such as K_2CO_3, Na_2CO_3, and Na_2SiO_3 may be used but in kaolin refining, ordinary potash alum, $KAl(SO_4)_25H_2O$, is found most satisfactory.

An interesting experiment would consist in drying this

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fire clay at various temperatures after a limited weathering. Some number two fire clays work much more satisfactorily in the filter press after once being dried at 100° to 120° C.

Prof. Bleininger: From the note of Mr. Thomas, it would appear that the longer weathering results in a coagulated condition of the clay, while the shorter exposure causes it to be in the deflocculated state. It would seem perhaps that the difference is due to soluble salts being formed from the pyrites in the clay. The amounts involved need be but very slight.

Prof. Binns: There are two possible reactions in the weathering of clay, either of which would account for the phenomena in question. Weathering involves both mechanical and chemical processes; the latter consist mainly in the breaking down of alkali-bearing minerals and the slow liberation of salts. The effect of the liberated alkali is first to suspend the clay in the mixing water and then to cause it to settle as more alkali is brought into solution. This would be accompanied, however, by a decrease in plasticity.

On the other hand, an acid reaction would equally well account for the settling of the clay, though not so well for the previous suspension. The acid reaction might arise from the liberation of sulphuric acid due to the oxidation of pyrite and subsequent separation of limonite, or it might be due to organic growth. The increase of plasticity in aged clay has been shown by Stover to be due to bacterial growth and this is believed to set up an acid reaction. Seger produced a similar effect by the addition of an acid. It would not be difficult to determine which of the two causes was operative.

The phenomenon at the filter press is simply incidental to the decomposition or weathering. In the half weathered clay the finer particles are liberated. These pass to the inner face of the cloth and form the waterproof coating. On prolonged weathering the whole clay is broken down and the non-plastic particles are also set free. These mingle mechanically with the fine plastic grains and produce a mixture which is sufficiently porous to allow the whole mass to be filter-pressed.

As to the matter of accelerating the reaction, three things are possible: 1. The addition of a weak acid. 2. The addition

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of an alkali. 3. The inoculation of the new clay with some already weathered. These suggestions are simply tentative. Experimental work alone would determine which, if any, were effective.

Mr. R. T. Hipp: The several conditions mentioned in Mr. Thomas's paper, "Settling and Filtering of Fire Clays," have been noted with interest, and are subjects that have been given considerable thought and extensive research by manufacturers of washed clays.

During my association with a concern which was weathering and washing pot clays, I experienced conditions similar to those outlined by Mr. Thomas. A clay which will settle rapidly in the tank, and will permit of easy filtration through the press (leaving the press cloths comparatively clean) is a clay which has been exposed to the weather a sufficient length of time so that a large percentage of the very desirable milk or colloidal matter is lost, being washed away by the rains and leaving a large content of a somewhat insoluble matter.

A clay which has not been weathered to any great extent or for a sufficient length of time to remove the colloids, will, of course, permit them to become dissolved in the stirring tank. It is this milk found in fresh clay that stays in suspension in the settling tank, and a small percentage adheres to the cloths in the press, the balance passing off in the waste water.

The troubles that confront the clay washer are ones that, unfortunately, can be remedied only at the expense of the consumer. This is due to the fact that the manufacturer can weather his clay more completely at a trifling cost thus driving out the valuable colloid matter before this clay reaches the wash-house, and the consumer is forced to use an article much inferior in quality as compared with what this same clay would be if it were merely weathered for several months and not washed.

It is conceded beyond all question that the most valuable clays for glass-house refractories come from Germany, and this condition will certainly continue to exist as long as our native clays are placed on the market with their most valuable property, *i. e.*, colloid matter, removed by washing.

Mr. C. W. Berry: Since establishing our laboratory some

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seven years ago, our process of working clay has been changed and improved continually until we have developed a wonderful tensile strength and plasticity in our washed clays.

Our method has consisted of carefully picking the clay as it comes from the mine, then placing it on the weathering piles where it is distributed over a large area in thin layers; the clay is weathered from three to five years and is worked continually during this period by men with rakes, raking down the sides of the piles as the clay is used. The clay when taken from these weathering piles to the washing tubs should be in a fine state of disintegration; if it is not and there are lumps remaining, the clay should be put through a pan or disintegrator before going into the tubs.

We believe too much care can not be given to the selecting of clays as they come from the mines and even in the mines; the dark top clay is usually the best and should be shot down separately and when carefully picked before going on weathering piles.

There are bad streaks of faulty clay in some of the mines and those should never be used for washing purposes, but can be made up into common fire brick. This sandy hard clay occurs more often in the locality known as the "Cheltenham" district than it does in the mines of the "Oak Hill" district; in fact, there is very little of the dark upper strata of pot clay found in the Cheltenham district.

We have only one satisfactory way of testing the plasticity and tensile strength of our clays and that is by actual test with a tensile strength machine as is used in testing cement. We test our washed clays every few days, both raw and burnt, modifying our process of washing when we find the tensile strength diminishing.

We know the high tensile strength of our washed clay is obtained simply through the care exercised in its selection and preparation.

Mr. C. H. Kerr: From the studies which have been carried on by various investigators it is very clear that the colloidal condition of the plastic constituents of a clay is of the utmost importance in determining the physical properties of the clay.

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Ashley[1] has made a searching review of the literature bearing upon this subject and he has given a very brief, but very clear, summary of the work. This question of the effect of weathering is another phase of the same problem.

Mr. Thomas brings to our attention the fact that a Missouri fire clay when not well weathered will remain in suspension for a long period of time and when it does settle will leave a milky suspension in the water above. The same clay when weathered for a sufficient period of time will settle rapidly leaving a clear water above. There can be no question that this milky suspension which refuses to settle is colloidal and that the alterations produced by weathering must effect the colloidal condition of the plastic constituents of the clay.

It has long been known that the addition of small amounts of electrolytes to clay suspensions would produce very marked effects. Ashley[2] has cited a number of such instances and Wiley[3] has given certain others.

In these various investigations it has been found that the addition of small amounts of certain electrolytes to certain clays will produce a flocculation or precipitation of the clay slip while larger amounts of the same electrolytes will produce a subsequent deflocculation or suspension of the slip. With other electrolytes small additions cause deflocculation while larger additions flocculate or precipitate the slip. Still other electrolytes will produce flocculation and others deflocculation of the slip as larger proportions are added. Mellor, Green and Baugh[4] made a very complete study of the effect of adding certain materials to a slip made from an earthenware body containing ball clay 23.53 per cent., china clay 27.95 per cent., Cornish stone 19.11 per cent. and flint 29.41 per cent. They summarized their conclusions as follows:

"The different substances may be arranged in five groups:

"1. Substances which first make the slip more fluid while

[1] Ashley, H. E., "The Colloid Matter of Clay and Its Measurement," Bull. 388, U. S. Geol. Survey (1909). Also Trans. A. C. S., Vol. XI, pp. 530–95.

[2] Ibid.

[3] Wiley, H. W., "Principles and Practice of Agr. Analysis," Vol. I., pp. 181–95 (1906).

[4] Mellor, J. W., Green, S. A., and Baugh, T., Trans. Eng. Ceram. Soc., Vol. VI, pp. 161–70.

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further additions stiffen the slip. Examples: sodium and potassium carbonates, fusion mixture; potassium sulphate; potassium bisulphate; potassium hydroxide; potassium nitrate; sodium sulphide; tannin and gallic acid.

"2. Small amounts thicken the slip, increasing amounts made the slip more fluid. Examples: copper sulphate, dilute ammonia, and potassium aluminium sulphate.

"3. Substances which make the slip thinner. Examples: magnesium, mercury and sodium sulphates; sodium sulphite; sodium acetate; sodium chloride; sodium phosphate; ammonium gallate; hydrochloric acid; water glass. It is just possible that some of these substances may have to be transferred to the first (or second) group if greater (or less) concentrations be tried than those employed.

"4. Substances which only stiffen the slip. Grape sugar, humic acid, borax, ammonium chloride, calcium chloride, calcium sulphate, ammonium urate, aniline, ethylamine, methylamine. Here again some of these substances may have to be transferred to the second (or first) group if greater (or less) amounts than those just indicated are used.

"5. Substances which have no appreciable effect on the slip; e. g., alcohol."

The clay to which Mr. Thomas refers contains about 0.1 per cent. of K_2O and Na_2O which is probably there in the form of undecomposed feldspar. During the weathering this feldspar is decomposed to a greater or less extent, yielding the alkalies in carbonate form. In this way changes are brought about in the electrolytes present in the clay slips. Such changes must cause, or help to cause, flocculation and consequent settling of the "sol" form of the colloids present in the unweathered or partly unweathered clay.

If a few drops of a normal solution, as hydrochloric acid, be added to 100 cc. of a thin slip of this clay in the partly weathered state, the clay will be found to flocculate and settle rapidly, whereas a similar sample of the same clay without the addition of the electrolyte will remain in suspension for several days without settling appreciably. The same is true of the milky white suspension which remains above the partly weathered

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clay after it has finally settled; a single drop of a normal solution of hydrochloric acid will cause a very rapid flocculation and settling of this colloidal material which before the addition of the electrolyte had remained in suspension for several months. The addition of a few drops of a normal solution of sodium carbonate to 100 cc. of thin slip of the partly weathered clay causes no flocculation, the clay remaining in suspension like the untreated sample. An excess of the sodium carbonate, however, flocculates and settles the slip. With sodium chloride a few drops of normal solution causes flocculation and precipitation which is contrary to the finding of Mellor, Green and Baugh in working with the earthenware body.

In addition to the precipitation of the suspended colloids by small amounts of electrolytes formed during the weathering, it is evident that the weathering must cause changes in the colloidal condition of the clay particles. The alternate expanding and contracting, wetting and drying, etc., must produce very profound changes in the physical condition of the material. Hydrolysis undoubtedly plays an important rôle, and it seems a well established fact that colloidal forms of aluminum silicates, silicic acid, and hydroxides of iron and in some cases of aluminum may be and are formed when the clay is exposed to weathering agencies.

It is very probable that in addition to these two causes, (1) the action of electrolytes in flocculating and precipitating the colloids and (2) the changes in physical condition of the clay due to the mechanical processes operative during weathering, there are also other agents at work which produce more or less important alterations.

A thorough and careful study of the changes which take place during the weathering of a hard and rock-like clay should prove of great moment in helping to solve the problem of that elusive property, plasticity.

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BODIES FOR INVERTED MANTLE RINGS.[1]

By R. LINN CLARE, Columbus, Ohio.

INTRODUCTION.

Inverted mantle rings are white porous bodies, used as the supporting frames for the frail mantles on inverted, illuminating gas burners. They are also a means of attaching the mantles to these burners by three lugs extending from the rings.

The problem in this investigation was to make such experiments as would show, if possible, what combination of materials and what treatment of these materials would produce a good, commercial mantle ring. It would seem at first thought that this should be fairly easy, but upon investigation of the subject, the writer found that such was not the case as is shown by the following work. This problem was suggested by the fact that one Ohio firm was forced to quit manufacturing inverted mantle rings because it was unable to secure more of the materials used in their body mixture and was unable to obtain another successful formula to replace the one it had been using. This problem was also suggested because of the absence of any literature on the subject, due no doubt to the fact that firms manufacturing the rings are loth to give any information regarding same.

EXPERIMENTAL WORK.

PRELIMINARY STEPS.

The first work was to determine to what temperature changes the rings were subjected. Consequently, an inverted burner was set up in the laboratory with mantle and ring attached, and by means of a standardized thermo-couple the hottest point in the lighted burner was found to be 860° C. The writer noticed, however, that the rings never attained a red heat, due probably to the rapid radiation losses. The hottest point in an open "Bunsen" burner was found to be 1000° C. These data suggested that it was not necessary to give much thought to the refractoriness of the ingredients used.

Tests were then performed on various commercial mantle

[1] Abstract of a thesis done under the direction of Professor R. C. Purdy, in the Ceramic Engineering Laboratories of the Ohio State University.

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rings, chemical porcelains such as casseroles and crucibles, and thermo-couple tubing. These tests were made by heating portions of the pieces to redness in a gas and air blast, keeping the other portions out of the flame, and then cooling the piece suddenly either in air or by dropping into cold water. It was found that under this intensive treatment the chemical porcelains and the thermo-couple tubing ruptured much easier than the commercial mantle rings. This warned the writer against using bodies of the chemical porcelain type.

From such preliminary work and from advice received from persons interested in this subject, the writer decided upon the following requirements for a commercial mantle ring:

(1) It must stand sudden and repeated changes of temperature without rupture.

(2) It must be white after burning.

(3) It must be of good mechanical strength, green and dry.

(4) It must have sufficient bonding ingredients to be workable by the dry-press process.

From the above, the writer decided that a porous body, the cementing bond of which had a low coefficient of expansion when vitrified, would probably serve the purpose. Upon investigation, however, it was found that chemical porcelains made up on the formulae of bodies of the lowest coefficient of thermal expansion found by Purdy and Potts[2] were not satisfactory; that is, they did not stand the sudden changes in temperature as well as other bodies of higher coefficient. The writer was also advised by Mr. Earl T. Montgomery, who has made some investigations along this same line, that the introduction of flint or feldspar into the body mixtures for inverted mantle rings gave rise to difficulties that precluded their use.

As a result it was decided to totally disregard the coefficient of expansion of the materials used and to omit flint and feldspar in the bodies of the series devised.

THE INVESTIGATION PROPER.

The Compositions Tested.—The separate series were therefore devised to contain: first, a constant amount of ball clay

[2] Trans. A. C. S., Vol. XIII.

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to furnish the vitrified bond; second, varying amounts of a refractory kaolin; and third, varying amounts of some non-plastic grit. This was to give a porous body with the ball clay acting as the vitrified bond. In the different series, different non-plastics were used, as shown in Table I.

TABLE I.—COMPOSITIONS TESTED.

Series A.—(Calcined kaolin)				Series B.—(Calcined $MgCO_3$)			
No.	Ball clay	Kaolin	Calcined kaolin	No.	Ball clay	Kaolin	MgO
1	15	70	15	0	15	77·5	7·5
2	15	60	25	1	15	70	15
3	15	50	35	2	15	60	25
4	15	40	45	3	15	50	35
5	15	30	55	4	15	40	45

Series C.—(100-mesh alundum)				Series D.—(200-mesh alundum)			
No.	Ball clay	Kaolin	100-mesh alundum	No.	Ball clay	Kaolin	200-mesh alundum
1	15	70	15	1	15	70	15
2	15	60	25	2	15	60	25
3	15	50	35	3	15	50	35
4	15	40	45	4	15	40	45
5	15	30	55	5	15	30	55

Materials Used.—The ball clay was "English ball clay No. 12," purchased from The Golding Brothers Company of East Liverpool, Ohio. It is very plastic, vitrifies slowly at about cone 9 to 10, and burns white. This particular clay was selected as the bond because its properties were best known to the writer.

The kaolin selected was "Dillsboro kaolin" mined by the Harris Clay Company at Webster, North Carolina. It is somewhat plastic and burns white. Incipient vitrification begins at about cone 11 to 12. Its drying shrinkage is six per cent.; burning shrinkage, four per cent.; sp. gr., 2.43. The analyses of this clay as given in the North Carolina Geological Survey[3] are as follows:

[3] Bulletin No. 13, "Clay Deposits and Clay Industries in North Carolina."

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Ultimate analysis		Proximate analysis	
Moisture	0.35	Clay substance	96.81
Silica	45.70	Quartz	0.07
Alumina	40.61	Feldspar	3.12
Ferric oxide	1.39		
Lime	0.45	Total	100.00
Magnesia	0.09		
Alkalies	2.82		
Water (loss on ignition)	8.98		
Total	100.39		

This clay was selected primarily because of its low fire shrinkage. This would tend to lessen the loss during firing. It was also chosen for its good color after firing. Of course other kaolins of this type would serve as well, but this one was the best available at the time.

The calcined kaolin was the above mentioned Dillsboro kaolin calcined in a small gas-fired muffle kiln to cone 3. This was then ground in a ball mill to pass a one hundred mesh screen or finer. This non-plastic was selected because of its cheapness and because of the simplicity it gave to the formula.

The magnesium oxide was secured by calcining commercial magnesium carbonate in a gas-fired muffle kiln to cone 3. This suggested itself as a cheap, refractory non-plastic and was used because of the fact that a chemical analysis of one commercial mantle ring showed it to be high in MgO.

The 100-mesh alundum (which is the trade name for fused bauxite or corundum) was secured from the Norton Company of Niagara Falls. Analysis shows SiO_2, CaO and MgO to be present but in such small quantities as to be negligible. This grit was suggested because of its use in chemical porcelains, and because it is an excellent refractory. It has little or no fire shrinkage and a coefficient of expansion nearly like that of the average ball clay.

The 200-mesh alundum is the same as the above, only ground finer. The use of the varying sizes of grain was to ascertain if possible the size best in respect to working properties and to the properties of the finished product.

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All of the above non-plastics will burn white.

Preparation of the Bodies.—Each body was blunged from fifteen to twenty minutes in a small hand power blunger of three liters capacity. Sufficient water was added to each body to bring it to a smooth slip, thick enough to prevent settling of any of the components. The only difficulty encountered in the process was with the magnesium oxide series. This entire series had to be passed through a one hundred mesh screen and be re-blunged in order to break up the flocculated particles of MgO.

After blunging, all the bodies were passed through a one hundred mesh screen to take out any foreign materials and then dried.

After drying, each body was ground to pass a twenty mesh screen. Next they were spread separately on muslin-covered slabs and approximately ten per cent. of water was sprayed on each. They were then placed in a small plaster-lined damp-box for aging. The bodies remained there four days in order to allow the moisture added to become uniformly distributed and to secure any added bond that might result from aging the plastic ingredients.

Making the Rings.—After numerous attempts, the writer was unable to secure either a commercial mantle ring press or a mantle ring die. The problem then resolved itself into securing a shape and size for the trials suitable for getting a reliable test. It was finally decided to adopt a simple ring of rectangular cross-section. This ring was to have a diameter the same as that of the commercial ring and a cross-sectional area approximately that of the smallest cross-section of the commercial ring. This discussion was the result of many tests of commercial rings. It will be noticed that there are no lugs on this ring, nor has it exactly the same shape in cross-section that a commercial ring has. The lugs were omitted for two reasons: first, because it was noted from the tests that the presence of the lugs on the ring weakened it in no way but in most cases seemed to give added strength. The rings always ruptured through the section of least area. The rectangular cross-section was adopted because of the simplicity it gave to the die construction and because at the same time it was in no way stronger than the commercial ring

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with the rounded cross-section. A die was designed to make a ring according to the above and when finished it was simple in construction and in manipulation. A top plunger compressed the circular hollow column of clay and a bottom plunger pushed out the ring. The die was fitted upon a small hand-power lever press capable of exerting sufficient pressure to give a good bond to the dry-pressed rings. The dimensions of a green ring were as follows: inside diameter $1^3/_{32}$ in., outside diameter $1^3/_8$ in., thickness of ring $^9/_{64}$ in., height of ring $^3/_{16}$ in.

Each ring received approximately the same pressure and all were exactly the same size. A measured amount of material was made into each trial so that no ring contained any more or less material than any other of the same body composition. This was easily controlled, for the height of column compressed could be varied at will.

Each body was re-screened through a twenty mesh sieve just before using. This broke up any lumps present and gave a still more even distribution of moisture.

Each ring was given two pressures in the press, the first to expel the air and the second to complete the bond. All the bodies worked well by this method and had good mechanical strength, both green and dry. The rings could be handled with safety and in no instance was a ring broken except by extremely rough handling.

Those bodies high in alundum were very hard on the die. Their abrasive nature would require frequent replacement of dies in commercial practice.

Sixty rings were made from each body and allowed to dry thoroughly in air, on metal palettes. All dried safely. No marks or scratches of any kind were put on the rings, but each body was placed on a separate marked palette as a means of distinguishing them.

Burning the Rings.—The rings were piled four high in small saggers and surrounded on the outside by clean sand to prevent their becoming displaced. Care was taken not to get any sand within the rings lest it prevent their shrinking freely. Small pieces of porcelain, marked with the different body numbers, were placed within each set of rings as a means of distinguishing

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the various members after burning. Eight rings of each body were set in each different burn; the saggers were wadded to prevent the kiln dust marring the rings; and cones were placed in each to indicate the exact heat treatment received.

The different burns were made in the small, coke-fired, downdraft, test kilns in use in the Ceramic Laboratory of the Ohio State University. Kiln No. 1 has two furnaces and its chamber is 4′ 4″ × 2′ 0″ × 2′ 4″ high. Kiln No. 3 has one furnace and its chamber is 2′ 0″ × 2′ 0″ × 2′ 4″ high. The cone 8 and cone 10 burns were made in kiln "No. 1." The cone 12 burn was made in kiln "No. 3." The finishing temperature in each burn was reached in 45 hours and the burns were uniform in all the saggers. All the kilns were allowed to cool slowly with wickets up. Cone 12 was about the highest temperature obtainable in these kilns with the fuel available and, therefore, no attempt was made to burn at a higher cone. When removed from the saggers all the rings had a good white color, were porous, and none were cracked or broken.

Testing the Rings.—The adoption of a suitable test for these rings was a matter of some investigation. They required a test intensive enough to break them yet somewhat similar to the conditions under which they are used. The chemical porcelain test, that is, heating up the piece and immersing it in water, was obviously out of the question, because once the ring was immersed it would instantly become saturated with water and any subsequent heating would rupture the ring, owing to the sudden expansion of the steam formed. The time at hand was not sufficient to permit of drying the ring after each test. The following test was finally adopted and proved to be entirely satisfactory.

The Test.—One-half of the ring is heated in the hottest part of a gas and air blast lamp and almost instantly becomes white hot. The ring hangs on a small wire hook during the heating process. Then it is grasped with tongs and placed directly in a cold air blast, which chills the ring rapidly. Finally it is placed on the hook of a spring balance and subjected to a pull of six pounds. The pull of six pounds was found to break any ring that had a slight crack, yet not sufficient to break a sound

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TABLE II.—RESULTS OF TESTS.

Series A.—(Calcined kaolin)				Series B.—(Calcined $MgCO_3$)			
No.	Cone 8	Cone 10	Cone 12	No.	Cone 8	Cone 10	Cone 12
1	4	10 H	10 H	0	10 H	10 H	10 H
1	5	10 H	10 H	0	9	10 H	10 H
1	2	10 H	10 H	0	7	10 H	10 H
2	3	10 H	5	1	3	10 H	10 H
2	10 H	2	5	1	2	9	10H
2	10 H	1	5	1	3	10 H	10 H
3	4	10	2	2	0	0	4
3	8	5	10 H	2	0	0	0
3	10 H	1	10 H	2	0	0	0
4	4	9	2	3	0	0	0
4	1	1	4	3	0	0	0
4	1	10 H	10 H	3	0	0	0
5	6	1	10 H	4	0	0	0
5	10 H	5	10 H	4	0	0	0
5	1	7	3	4	0	0	0

Series C.—(100-mesh alundum)				Series D.—(200-mesh alundum)			
No.	Cone 8	Cone 10	Cone 12	No.	Cone 8	Cone 10	Cone 12
1	10 H	10 H	10 H	1	10 H	10 H	10 H
1	10 H	10 H	10 H	1	10 H	10 H	10 H
1	10 H	10 H	10 H	1	10 H	10 H	10 H
2	10 H	10 H	10 H	2	10 H	10 H	10 H
2	10 H	10 H	10 H	2	10 H	10 H	10 H
2	10 H	10 H	10 H	2	10 H	10 H	10 H
3	10 H	10 H	10 H	3	10 H	10 H	10 H
3	10 H	10 H	10 H	3	10 H	10 H	10 H
3	10 H	10 H	10 H	3	10 H	10 H	10 H
4	10 H	10 H	10 H	4	10 H	10 H	10 H
4	10 H	10 H	10 H	4	10 H	10 H	10 H
4	10 H	10 H	10 H	4	10 H	10 H	10 H
5	10 H	10 H	10 H	5	10 H	10 H	10 H
5	5	2	10 H	5	10 H	10 H	10 H
5	9	10 H	10 H	5	10 H	10 H	10 H

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ring. Although the commercial ring is never subjected to any tension in practice, it was found that this was a ready means of discovering cracks too small to be seen with the naked eye. The above procedure is repeated with each ring up to ten times. If it fails then to break, the ring is given a mark of "10 H" (10 Held) and is considered one capable of standing the hardest commercial usage. The writer feels fairly safe in making this last statement, because out of many commercial mantle rings tested in this manner, only two stood the test ten times and the others failed at varying points from one to nine.

It will be noticed that this test is intense in every respect. The temperature of the blast used was found to be 1330° C., while that of the ordinary illuminating gas burner is only 860° C. The heat was always applied to the same portion of the ring in these repeated tests. This was designed to set up additional strains and to open any microscopical cracks that might be formed.

Results of the Tests.—The results of the tests are shown in Table II. The numbers show how many times the rings stood the test without failure. Three rings of each body from each burn were tested.

Discussion of Results.—Series "A". It is noticed in this series that at cone 8 all of the bodies are unreliable, that is, it seems a matter of accident whether or not a good ring is obtained.

At cone 10, A1 is undoubtedly a good ring for all three bodies held after ten tests. However, with increasing percentages of calcined clay, the rings become less and less reliable, yet as a whole they are better than those of the cone 8 burn.

At cone 12, A1 is still a good ring, with all the other members still unreliable yet slightly better than those at cone 10.

Series "B." It is noticed that the cone 8 burn of this series is unreliable throughout all the members.

At cone 10, B-0 is a successful ring and B-1 very nearly so.

At cone 12, both B-0 and B-1 are entirely successful rings.

The most notable thing about this series is the very high fire shrinkage, due no doubt to the high MgO, as the shrinkage increases with increased MgO. Another notable fact about these rings is that those bodies with over twenty-five per cent. of MgO have not the mechanical strength after burning to

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stand the six pounds tension. They were easily broken, even without heating, and for this reason none of these were considered.

Series "C." This series was entirely successful except for member C-5 at cones 8 and 10. This member, however, became a successful ring at cone 12.

The one objection to this ring was the fact that the one hundred mesh alundum gave the ring a rough, gritty, appearance in the higher members. These members were also very hard on the die.

Series "D." This series was successful in all particulars. It had good color, good general appearance, worked well in the die, and stood the tests perfectly at all cones.

CONCLUSIONS.

(1) This investigation proves conclusively that successful commercial inverted mantle rings can be made, using either two hundred or one hundred mesh alundum as the grit in the bodies, and burning to cones 10 or 12. The two hundred mesh alundum used as the grit gives a better ring, as to general appearance and strength, than does the one hundred mesh.

(2) Calcined Dillsboro kaolin used as the grit is unsatisfactory when in amounts greater than fifteen per cent. and when the bodies are burned lower than cone 10. This ring has the advantage, however, of being the cheapest ring to produce.

(3) Calcined magnesium carbonate, used as the grit in the bodies, gives successful rings when in amounts of twenty-five per cent. or less. This material has the disadvantage of introducing a very high fire shrinkage.

(4) English ball clay "No. 12" is eminently successful as the vitrified bond for inverted mantle ring bodies burned above cone 8.

(5) Dillsboro kaolin is a very good white refractory ingredient for the major portion of the inverted mantle ring body.

(6) A consideration of the coefficient of expansion of the materials in the thermal treatment of such bodies seems unnecessary.

(7) All the compositions used worked well in the die, had

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good mechanical strength, green and dry, and burned to good white bodies.

(8) Bodies of the compositions used should be burned above cone 8 for best working strength. The ability of the bodies to resist the test imposed, increased with increased heat treatment up to cone 12.

ACKNOWLEDGMENT.

The writer wishes to acknowledge the many helpful suggestions and the valuable advice received, while carrying on this investigation, from Professor Ross C. Purdy, Mr. Arthur S. Watts, and Mr. Earl T. Montgomery.

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LIGHT GREEN CHROMIUM STAINS.

By A. R. HEUBACH, Alfred, N. Y.

INTRODUCTION.

Seger gives the following formula for a brilliant light green stain, so-called "Victoria Green:"

36	Potassium bichromate
20	Flint
12	Fluorspar
20	Whiting
12	Calcium chloride (molten)
100	

The writer has used this stain repeatedly as a coloring for terra cotta glazes at cone 3 as well as cone 7, with equally good results.

However, with the large amounts of stain needed in this line, the writer found it very annoying to handle large quantities of both potassium bichromate and calcium chloride, the former on account of the fine dust which spreads all over the room and is very irritating to nose, throat and lungs, the latter on account of its property to absorb moisture from the air eagerly, which makes it sticky and hard to grind.

Seger used with these ingredients in solution, but that also would be a difficult matter on a large scale, and as the total batch would have to be reground after evaporation in order to get a thorough mixture, the same inconveniences would be experienced as in mixing and grinding dry. Seger's purpose in using the solutions was to get a better distribution of these compounds.

I tried both the solution method and grinding of the materials dry, and, in my experience, there is no noticeable difference, provided the materials are ground fine enough.

The object of this investigation was to produce a stain of equal brilliancy and intensity by substituting for the bichromate and the calcium chloride other compounds which can be easily handled in large quantities.

As a first step, it was decided to determine the influence of calcium chloride and other calcium compounds in regard to color and stability of the stains.

It was intended to select the most promising members of

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this investigation; and if it should be found that calcium chloride was essential to the development or stability of the color, the substitution for calcium chloride of combinations such as whiting and salt in equivalent amounts was planned.

As a last step the potassium bichromate was to be replaced by chromium oxide and nitre, or possibly both calcium chloride and bichromate by whiting, chromium oxide and salt in equivalent amounts.

PART I.—THE INFLUENCE OF LIME COMPOUNDS AND REPLACEMENT OF CALCIUM CHLORIDE BY OTHER LIME COMPOUNDS.

In planning the investigation, I intended at first to use equivalent amounts of the lime compounds; but as my previous experience with these stains seems to show that the color depends on the form in which the lime is present, rather than the amount of lime as such, and as I desired to include Seger's stain in this investigation to facilitate comparison, I finally decided to use percentage amounts. Seger does not use equivalent amounts and therefore it would have been impossible to include his stain in the investigation.

As Seger's stain contains three lime compounds, the triaxial diagram suggested itself, and I used it in the following manner with Seger's formula as a basis:

Seger's formula contains 36 per cent. potassium bichromate and 20 per cent. flint, which were kept constant throughout. The remaining 44 per cent. were made up by lime compounds. As some authors recommend the use of plaster of Paris for light green stains also, I decided to include this compound in this investigation.

The following four extremes were made up, and three of them blended with each other in four stages:

	A	B	C	D
Potassium bichromate	36	36	36	36
Flint	20	20	20	20
Fluorspar	44	..	..	..
Calcium chloride	..	44	..	..
Whiting	..	..	44	..
Plaster of Pari	..	..	..	44
	100	100	100	100

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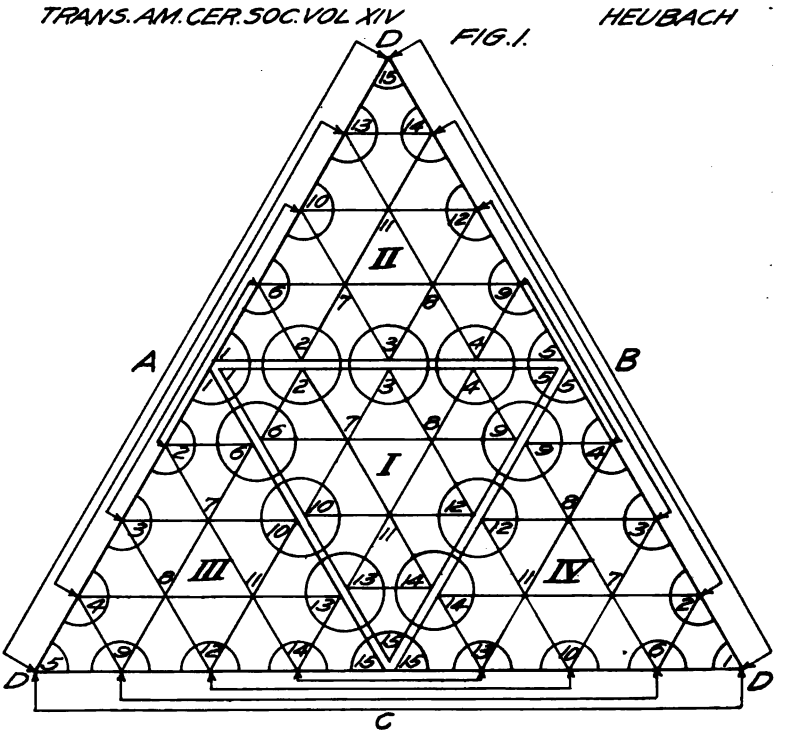
These mixtures were ground dry in a ball mill for two hours and passed an 80-mesh screen without residue. They were then blended as indicated in the diagram. The mixture B was kept in an air-tight jar, which was opened only for each weighing.

In order to include the four extremes in the triaxial diagram, I placed the mixture D at the three corners of the triangle, and the mixture A, B and C in the middle of the sides.

I thought, however, that this arrangement might be too complicated for those who cannot read the triaxial diagram readily, and for this reason I divided the triangle into four smaller ones, each representing a separate group.

No. 11, in Group I, does not correspond exactly to Seger's formula, but the color is identical, and therefore this stain represents the standard.

This method has the disadvantages, that some of the mix-



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tures will reoccur in different groups. Fig. 1 shows the diagram with the four subdivisions; the duplicate mixtures are indicated by circles and semi-circles. This triaxial diagram has appeared so frequently in the Transactions of this Society that a further explanation seems unnecessary.

For the benefit of the practical men, who are not able to read the mixtures from the diagram, I will give the actual weights of each stain. See Table I:

TABLE I.—COMPOSITION OF STAINS.

Group I	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Potassium bichromate	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Flint	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Fluorspar	44	33	22	11	..	33	22	11	..	22	11	..	11	..	..
Calcium chloride	..	11	22	33	44	..	11	22	33	..	11	22	..	11	..
Whiting	..	..	..	..	..	11	11	11	11	22	22	22	33	33	44
Group II															
Potassium bichromate	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Flint	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Fluorspar	44	33	22	11	..	33	22	11	..	22	11	..	11	..	..
Calcium chloride	..	11	22	33	44	..	11	22	33	..	11	22	..	11	..
Plaster of Paris	..	..	..	..	..	11	11	11	11	22	22	22	33	33	44
Group III															
Potassium bichromate	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Flin	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Fluorspar	44	33	22	11	..	33	22	11	..	22	11	..	11	..	..
Whiting	..	..	..	..	..	11	11	11	11	22	22	22	33	33	44
Plaster of Paris	..	11	22	33	44	..	11	22	33	..	11	22	..	11	..
Group IV															
Potassium bichromate	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Flint	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Calcium chloride	..	11	22	33	44	..	11	22	33	..	11	22	..	11	..
Whiting	..	..	..	..	..	11	11	11	11	22	22	22	33	33	44
Plaster of Paris	44	33	22	11	..	33	22	11	..	22	11	..	11	..	..

The stains were burned at cone 4, in an oxidizing atmosphere in cylindrical crucibles, which were not covered, in order to facilitate the escape of the volatile matter.

When the crucibles were taken from the kiln, a great number of them was badly cracked and apparently forced apart, while others appeared as if they had been soaked in a brown fluid.

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The latter is of course due to the volatile chromic acid and was particularly apparent with those mixtures which contain calcium chloride.

I am not able, however, to give a reason for the cracking of the crucibles. It is apparently due to an expansion of the stain, taking place at the earlier part of the firing, as all the stains, with the exception of numbers 10 and 13, in Groups I and III, formed small cylinders with about $^1/_4$ inch space between the stain and the wall of the crucible, as shown on the left of Plate I.

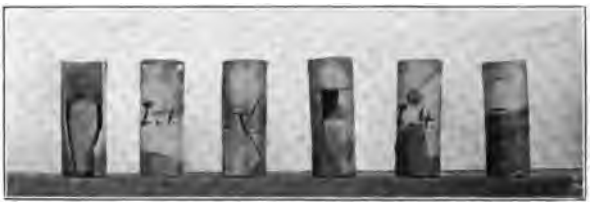

Plate I.

Numbers 10 and 13 had started to fuse and had boiled up to the top of the crucible.

The other five crucibles on Plate I show the cracks and the discoloration caused by the volatile compounds.

As an explanation for the fact that numbers 10 and 13 in Groups I and III are the only two stains which have actually started to fuse, while all the others were only more or less fritted, I would suggest the following:

B. Karandéeff[1] found the eutectic mixtures of calcium-metasilicate and calcium fluoride at 38.2 per cent. CaF_2 and 61.8 per cent. $CaSiO_3$ with a melting point at 1130° C.

Assuming that the whiting and the flint combine to calcium silicate, we find, by calculation, that No. 13 would contain 22.15 per cent. CaF_2 and 77.85 per cent. $CaSiO_3$; the whiting and flint happen to be present in equivalent amounts in this case, while No. 10 would contain 46.17 per cent. CaF_2 and 53.83 per cent. $CaSiO_3$ with some free silica, *i. e.*, leaving the bichromate out of consideration.

[1] Zeitschrift für anorganische Chemie, LXVIII, 3 (1910).

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Comparing these figures with the utectic mixture, we find that this would lie between No. 10 and No. 13, and that these two mixtures, being nearest to the eutectic, would therefore be expected to be the most fusible ones.

Karandéeff found also a eutectic mixture between calcium metasilicate and calcium chloride, with a melting point of 764° C. He does not give actual figures in this case, stating merely that the eutectic lies very close to the calcium chloride end. We would therefore expect signs of fusion between Nos. 5 and 9 of Groups I and IV, but this is not the case. However, the whiting being so low in these mixtures, there must be a considerable amount of free silica present, and this may have prevented the fusion. I state this merely as a suggestion and do not claim that it is actually the case.

The stains were then coarsely ground in a mortar and washed with hot water until the water was perfectly colorless. Washing the coarsely ground stains is much more convenient than grinding them fine first, as the stains will settle more easily, and the operation can be done more rapidly.

It developed that the amount of the soluble salts is inversely proportional to the amount of the volatile substances, *i. e.*, those stains which showed the strongest evidence of volatility needed only a few washings, while those which showed no or but little volatility had to be washed eight times or more before the water was colorless. The only exceptions to this rule were again Nos. 10 and 13, of Groups I and III. They did not show any pronounced evidence of volatility and yet the water was clear after three washings. This is due to the fact that they had fused and therefore did not give up the soluble salts readily. However, they had to be rewashed repeatedly after they had been finely ground, while none of the other stains needed rewashing.

The stains were then ground wet in a ball mill and screened through a 120-mesh screen.

In order to show the results plainly, little hexagonal tiles and parts of hexagonal tiles were made, which were arranged as shown in Fig. 2. Each screw which holds the tile to the board represents the point in the diagram at which the mixture of the stain, used on this tile, lies. Two series of these tiles were made.

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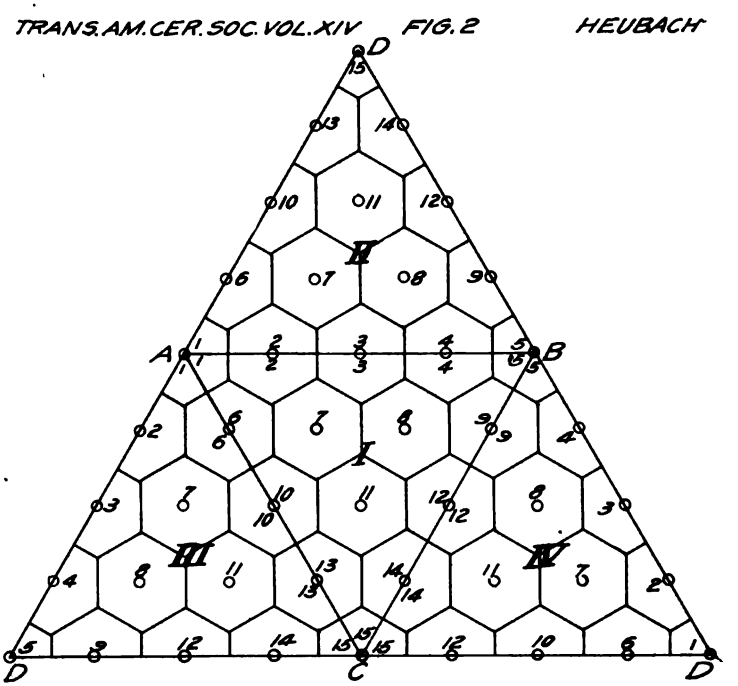

On one series the stains were used as under-glaze colors, to show the shade and intensity of the colors. This was done by mixing the stains in the proportion of 3 to 1 with a glaze of the following formula:

$$\left.\begin{matrix} 0.43\ CaO \\ 0.23\ K_2O \\ 0.34\ PbO \end{matrix}\right\} 0.25\ Al_2O_3 \quad \begin{matrix} 2.60\ SiO_2 \\ 0.31\ B_2O_3 \end{matrix}$$

which is the standard earthenware glaze of the New York State School of Clayworking and Ceramics. The same glaze was applied over the colors and the trials burned at cone 4.

There are little blisters and small spots bare of glaze on some of the tiles. This is not a defect of the colors or of the glaze, but is caused by the method of application. The colors were applied by spraying with plain water, consequently they were laying on the tiles as loose, dry powders by the time the glaze was applied. When the glaze was applied, the water of the glaze-slip

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expelled the air between the particles of the color, and this escaping air caused the glaze-slip to blister while it was being applied. This might have been avoided by simply using some gum with the under-glaze colors.

Other under-glaze colors are usually prepared by adding a few per cent. of ball clay or body mixture to the stain, and the gum may then be omitted. With delicate green colors, however, it is not advisable to use clay, as it produces brownish tints. To secure a proper bond between the body and the color, I used the addition of glaze, as otherwise the stain alone would act the same as dust on the ware.

The second series was made to test the stability of the stains, and to that end 5 parts of the stains were added to 100 parts of above glaze.

In this series the glaze has badly blistered on some tiles. As all the blistered glazes happen to contain plaster of Paris, it might appear, at the first glance, that the sulphuric acid from that source was causing the trouble. Perhaps it is indirectly the cause, but closer inspection reveals that, for instance, No. 9 of Group III, which contains 39 per cent. plaster, is perfectly smooth, also No. 8, which contains 22 per cent. plaster, while No. 2 of the same group, which contains only 11 per cent. plaster, has badly blistered. We find that all the glazes which show blistering have been applied too heavily, and I believe that, with the proper application, none of the glazes would show this defect.

The colors of the stains and of the under-glaze colors are shown in Table II.

The colored glazes of the second series have the same general appearance as the corresponding under-glaze colors, but the white body of the tiles, showing through the translucent glazes, makes the colors appear lighter. With a higher percentage of stain, to render the glazes opaque, the difference between the under-glaze colors and the colored glazes would probably be but slight.

The only distinct difference will be seen in No. 13 of Groups I and III. As under-glaze color this stain produces a grayish grass-green, while in the glaze it has been bleached to a pale

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TABLE II.—COLORS OF STAINS.

Color of stains in Group I			Color of stains in Group II		
No.	After washing	Under the glaze	No.	After washing	Under the glaze
1	Chromium green	Fair light green	1	Chromium green	Fair light green
2	Bluish chromium green	Chromium green	2	Bluish chromium green	Chromium green
3	Light chromium green	Darker than No. 2	3	Light chromium green	Darker than No. 2
4	Light chromium green	Darker than No. 3	4	Light chromium green	Darker than No. 3
5	Bluish chromium green	Dark olive green	5	Bluish chromium green	Dark olive green
6	Bluish chromium green	Grass green	6	Grass green	Grass green
7	Light grass green	Grass green	7	Chromium green	Dark chromium green
8	Light grass green	Chromium green	8	Light chromium green	Dark chromium green
9	Chromium green	Dark olive green	9	Bluish chromium green	Dark olive green
10	Brilliant light green	Good light green	10	Grass green	Chromium green
11	Brilliant light green	Standard light green	11	Chromium green	Dark chromium green
12	Dark olive green	Very dark olive green	12	Grayish chromium green	Dark olive green
13	Yellowish light green	Grayish grass green	13	Grass green	Dark chromium green
14	Dark green	Very dark olive green	14	Bluish dark green	Dark olive green
15	Grayish green	Brownish dark green	15	Grass green	Dark chromium green

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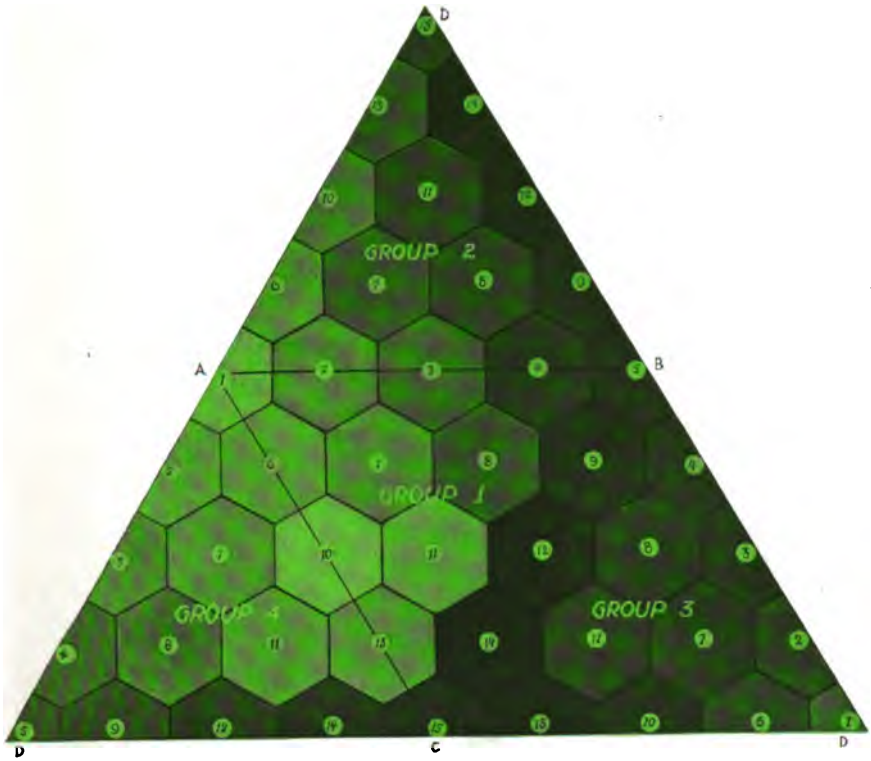

The plates accompanying this article indicate the differences in intensity of the colors produced, but not the differences in hue.

In the plate above, the triangle marked Group 3 should be marked Group 4, and vice versa.

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TABLE II (*Continued*).

	Color of stains in Group III			Color of stains in Group IV.	
No.	After washing	Under the glaze	No.	After washing	Under the Glaze
1	Chromium green	Fair light green	1.	Grass green	Dark chromium green
2	Grass green	Grass green	2	Bluish dark green	Dark olive green
3	Grass green	Chromium green	3	Grayish chromium green	Dark olive green
4	Grass green	Dark chromium green	4	Bluish chromium green	Dark olive green
5	Grass green	Dark chromium green	5	Bluish chromium green	Dark olive green
6	Bluish chromium green	Grass green	6	Chromium green	Dark olive green
7	Light grass green	Light chromium green	7	Dark chromium green	Olive green
8	Light grass green	Light chromium green	8	Chromium green	Olive green
9	Chromium green	Dark olive green	9	Chromium green	Dark olive green
10	Brilliant light green	Good light green	10	Chromium green	Very dark olive green
11	Brilliant light green	Like standard I 11	11	Grass green	Olive green
12	Chromium green	Very dark olive green	12	Dark olive green	Very dark olive green
13	Yellowish light green	Grayish grass green	13	Dark green	Very dark olive green
14	Dark green	Very dark olive green	14	Dark green	Very dark olive green
15	Grayish green	Brownish dark green	15	Grayish green	Brownish dark green

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TABLE II (*Continued*).

Color of stains in Group III			Color of stains in Group IV.		
No.	After washing	Under the glaze	No.	After washing	Under the Glaze
1	Chromium green	Fair light green	1.	Grass green	Dark chromium green
2	Grass green	Grass green	2	Bluish dark green	Dark olive green
3	Grass green	Chromium green	3	Grayish chromium green	Dark olive green
4	Grass green	Dark chromium green	4	Bluish chromium green	Dark olive green
5	Grass green	Dark chromium green	5	Bluish chromium green	Dark olive green
6	Bluish chromium green	Grass green	6	Chromium green	Dark olive green
7	Light grass green	Light chromium green	7	Dark chromium green	Olive green
8	Light grass green	Light chromium green	8	Chromium green	Olive green
9	Chromium green	Dark olive green	9	Chromium green	Dark olive green
10	Brilliant light green	Good light green	10	Chromium green	Very dark olive green
11	Brilliant light green	Like standard I 11	11	Grass green	Olive green
12	Chromium green	Very dark olive green	12	Dark olive green	Very dark olive green
13	Yellowish light green	Grayish grass green	13	Dark green	Very dark olive green
14	Dark green	Very dark olive green	14	Dark green	Very dark olive green
15	Grayish green	Brownish dark green	15	Grayish green	Brownish dark green

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grayish light green. It is apparently the least stable stain of the whole investigation, being partly decomposed by the glaze.

The color of No. 11, in Group III, may be regarded as identical with that of No. 11 in Group I, which is the standard color, and therefore the purpose of this investigation, to produce a color of the same general appearance as No. 11, Group I, without calcium chloride, has been accomplished.

Apparently, complicated reaction takes place in the formation of these stains, and as it is doubtful whether even a careful analysis would throw any light on this point, I shall refrain from any theoretical speculations.

CONCLUSIONS ON PART I.

The conclusions to be drawn from this investigation are as follows:

1. Fluorspar is essential for the production of light green stains.

2. Calcium chloride is not essential, acting merely as a modifier of the color.

3. Whiting alone does not give satisfactory results.

4. Whiting and calcium chloride and whiting and plaster of Paris produce very dark green colors.

5. Plaster of Paris acts very similar to calcium chloride as a modifier of the color.

6. The best results are obtained with a mixture of about equal parts of fluorspar and whiting, and this color may be modified by either calcium chloride or plaster of Paris.

It is understood, of course, that different glazes will give different results, particularly glazes of different temperature range. However, so far as glossy glazes of the same temperature range are concerned, the difference will not be noticeable, provided none of the glazes contain zinc oxide.

This is not so with matte glazes. An alumina matte, in an oxidizing burn, even if it does not contain zinc, will give brownish tints, or if green colors are obtained, they are very unreliable, changing with different burns or showing different tints even in one and the same burn.

On the other hand, in my experience, barium mattes produce very satisfactory results, provided they do not contain

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more than 0.1 equivalent of zinc oxide. One-tenth equivalent of ZnO will produce green colors, but they are as unreliable as the alumina mattes, while more than 0.1 equivalent of ZnO will invariably produce brown colors. This is in perfect harmony with Bryan's[2] results.

It seems, however, that zinc oxide is detrimental only when it is incorporated in the glaze, as I have produced good green stains with a considerable amount of zinc oxide in the stain.

Having demonstrated that calcium chloride is not essential in the production of light green stains, it remains only to substitute for the potassium bichromate some less objectionable compound.

To this end I shall select Group III as the only group which gave satisfactory results without calcium chloride.

PART II.—REPLACEMENT OF POTASSIUM BICHROMATE BY CHROMIUM OXIDE AND NITER.

In an endeavor to replace the objectionable potassium bichromate Group V was made up.

This group is the same as Group III with the exception that potassium bichromate was replaced by equivalent amounts of chromium oxide and nitre.

The three extremes are:.

	E	F	G
Chromium oxide	18.6	18.6	18.6
Niter	24.7	24.7	24.7
Flint	20.0	20.0	20.0
Fluorspar	44.0	...	...
Whiting	...	44.0	...
Plaster of Paris	...	...	44.0
	107.3	107.3	107.3

These were mixed according to the diagram and treated in exactly the same way as in the preceding groups.

The actual weights are given in Table III.

When taken from the kiln, the stains had very much the same appearance as those of Group III. Even Nos. 10 and 13, as in Group III, were the only two which had started to fuse.

[2] Trans. A. C. S., Vol. X, p. 124.

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TABLE III.—COMPOSITIONS OF STAINS.

Group V.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Chromium oxide	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
Niter	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7	24.7
Flint	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Fluorspar	44.0	33.0	22.0	11.0	....	33.0	22.0	11.0	....	22.0	11.0	....	11.0	....	....
Whiting	....	....	....	....	....	11.0	11.0	11.0	11.0	22.0	22.0	22.0	33.0	33.0	44.0
Plaster of Paris	....	11.0	22.0	33.0	44.0	....	11.0	22.0	33.0	....	11.0	22.0	....	11.0	....

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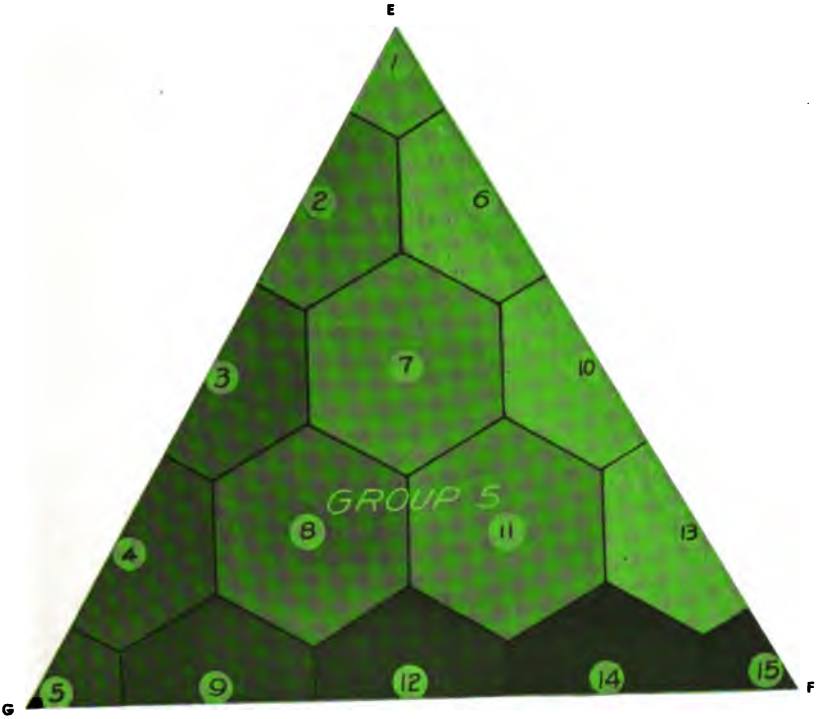

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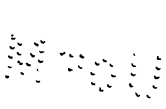

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Using the same glaze, the stains were applied to two series of tiles, as under-glaze colors, and as coloring matter in colored glazes.

The colors of the stains are shown in Table IV:

TABLE IV.—COLORS OF STAINS IN GROUP V.

No.	After washing	Under glaze
1	Chromium green	Light green
2	Chromium green	Grass green
3	Chromium green	Chromium green
4	Chromium green	Dark chromium green
5	Chromium green	Dark chromium green
6	Bluish chromium green	Light green
7	Grass green	Grass green
8	Grass green	Light chromium green
9	Chromium green	Dark olive green
10	Brilliant light green	Light green
11	Brilliant light green	Light green
12	Chromium green	Very dark olive green
13	Brilliant light green	Light green
14	Dark green	Very dark olive green
15	Grayish green	Very dark brownish green

The colored glazes have the same general appearance as the corresponding under-glaze colors. It might be mentioned, though, that they did not show the boiling up, which was observed in the preceding groups, as they were applied more carefully.

While the colors of this group show a striking similarity to the corresponding colors of Group III, many of them show a slightly different tint.

CONCLUSIONS ON PART II.

Strictly speaking, I did not succeed in matching Seger's "Victoria Green" exactly; however, the difference between Seger's "Victoria Green" and No. 11 of Group V is so slight that it would be negligible under factory conditions. If an exact match is desired, it could probably be secured by blending No. 11 with one of the other stains.

In order to avoid misunderstanding, I would say, in conclusion, that it was not expected that different lime compounds

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or chromium introduced from different sources would yield identical results.

In the case of the lime compounds we could not expect identical results, because they were not present in equivalent amounts.

Moreover, we have here what Dr. Mellor terms "arrested reaction," and even if the lime compounds had been present in equivalent amounts, we could not expect identical results.

In order to produce a certain result, we give the mixtures a certain heat treatment, *i. e.*, we do not permit of a complete reaction between the different ingredients, because if we did, we might get identical results, if the different compounds were present in equivalent amounts, with the exception of fluorspar, which would involve a variation of the silica content of the final product, but we would not get the light green color for which we were looking.

Since the original ingredients are different chemically as well as physically, the reaction is arrested at a different point in each case, although the heat treatment was the same in all cases. Therefore, we could expect identical results only, if we would bring the mixtures to complete fusion, and even hold them at that point for some time, to permit of a complete reaction, the same way as we do with a silicate fusion in chemical analysis.

The case is somewhat different with the chromium derived from different sources. Here we could reasonably expect similar results, because very likely the niter reacts with the chromium oxide, forming potassium chromate, at a temperature at which the other ingredients are still unaffected. It would then be only a question of the action of potassium bichromate in Group III and potassium chromate in Group V.

DISCUSSION.

Mr. Burt: I don't care particularly to discuss the use of chromium, because I have not worked very much with it. I think it is a very interesting line, and I am very glad to see it taken up and carried out, for we have not had very much work on the subject. I find that my best course is not to use chromium to a very great extent. I was interested to hear Mr. Heubach

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explain his trouble from blistering. That is very frequently the case.

Mr. Purdy: I wish to call attention to the fact made plain in these experiments, that the source of the oxides is am important consideration in the obtaining of tints. This is one of the points on which I have stood alone in chrome-tin stain discussions.

Mr. Pence: In replacing calcium chloride in Seger's formula with fluorspar or fluorspar and whiting, I find that the green color obtained is similar to that obtained from the Seger formula but that it is more yellowish and not so strong as the Seger green.

Unless the stain is used in very large quantities, Seger's method of preparation will not be found particularly inconvenient, and the stain obtained will be more satisfactory.

Mr. Heubach's statement concerning the action of the "Victoria Green" in the alumina matte does not agree with my experience. I have found the stain prepared from Seger's formula to give very reliable and uniform results in a matte of this type, the color being the green characteristic of the stain.

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KAOLIN MINING IN THE SOUTH APPALACHIAN MOUNTAINS.[1]

By A. S. Watts.

The following is a portion of an investigation carried on by the United States Bureau of Mines for the purpose of determining the industrial importance of the pegmatite dykes of the South Appalachian mountain districts and whether the variation in physical and chemical properties displayed by different portions of these dykes is inherent or is due to variation in refining processes.

The district covered by this investigation lies southeast of the full extent of the Great Smoky Mountains and consists of an immense tableland which extends from the Great Smoky range to the Blue Ridge mountains. The width of this plateau is more or less irregular owing to spurs from the Great Smoky mountains on the North and from the Blue Ridge on the south. Its maximum width, however, is about forty miles. The length of this plateau is approximately four hundred miles, including the gradual slope into Georgia at the southwest extreme and the slope into Virginia at the northeast extreme.

The pegmatite dykes which occur throughout this area are seldom of great width or extent but exist in vast numbers and apparently of considerable uniformity. Up to the present time the main products of these dykes have been mica and a limited amount of kaolin. The lack of transportation facilities has prevented more extensive mining of kaolin, feldspar and quartz, which are always encountered in the mining of mica within this area. Recent extensions of railroads have opened up additional areas within this district, and the time has arrived when their industrial value should be determined.

AREA COVERED BY THIS INVESTIGATION.

Starting at Rome, Floyd Co., Ga., and Dallas, Paulding Co., Ga., as the southwest extremes, the dykes producing the above materials follow a general northeast direction, becoming of commercial importance however only when the northeast slopes

[1] By permission of the Director, U. S. Bureau of Mines.

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of the Nantahala Mountains are reached. The dyke belt here broadens and covers the territory from Clayton, Rabun Co., Ga., to Brysen, Swain Co., N. C. Here the first kaolin mining in the belt was done. The belt narrows gradually until Waynesville, Haywood Co., N. C., is reached. Northeast of this point only small evidence of the dykes are found until Burnsville, Yancey Co., N. C., is reached. Here the belt expands to about twenty miles width, including the Spruce Pine, Penland and Bakersville districts, where operations are now quite extensive. Northeast of this district the dykes are less altered, only one dyke of kaolin of any value being found until the Virginia line is crossed. Beyond this line the dykes are scarce and of little value until Bedford Co., Va., is reached, where several important dykes are found producing both kaolin and feldspar. The investigation ended at Lynchburg, Va.

The Lower District.—The district northeast of Nantahala Mountains covers Macon, Jackson and Swain counties and a small amount of Haywood County. The dykes here are in an advanced state of kaolinization in most instances and are very numerous. In Macon Co., sixteen separate deposits of kaolin, three deposits of semi-kaolinized feldspar and five feldspar deposits were sampled. In Jackson Co., eleven kaolin deposits, three semi-kaolinized feldspar deposits and three feldspar deposits were sampled. In Swain Co., six kaolin deposits and one semi-kaolinized feldspar deposit were sampled. In Haywood Co., five kaolin deposits were sampled.

The Spruce Pine District.—This includes Yancey, Mitchell and Avery Counties.

The dykes in this district are in all stages of kaolinization. In Yancey County five kaolin deposits and two feldspar deposits were sampled. In Mitchell County eleven kaolin deposits, two semi-kaolinized feldspar deposits and eight feldspar deposits were sampled. In Avery County, two kaolin deposits and three feldspar deposits were sampled.

The other deposits studied lie outside these centers and may be considered in most cases as unimportant, although in a few instances these isolated dykes are of sufficient importance to justify operations.

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In a number of the most extensive deposits of this district the formation can hardly be recognized as dykes since the walls are not clearly defined and the deposit has no regular structure. Such deposits are undoubtedly great lenses formed at favorable positions along the intruded dyke. A fact worth noting in connection with these great lenses is that they are uniformly lower in feldspar and kaolin than are the better defined and narrower formations.

The material investigated are associated with or form a part of the granite pegmatites which occur throughout the Appalachian mountain range.

ORIGIN AND GEOLOGY.

A discussion of the origin and geologic occurrence of these dykes does not properly belong in this treatise. However, geologists agree that within the area covered by this investigation these pegmatites exist as dykes intruded into the enclosing rocks, probably in the fluid state; and because of the fact that such intrusion would naturally occur along the planes of easiest fracture, these dykes lack uniformity as regards both direction and size. They are lens-shaped, often pinching out within a few yards from a mass many yards wide to one only a few inches wide. The same is true of the perpendicular dimensions, although not to so pronounced a degree.

The majority of the dykes studied dip from 10° to 25° from the perpendicular toward higher ground of the present topography. The general direction of the dykes is northeast and southwest, but many of the large deposits appear to have a due north or due east direction.

The entire area covered by this investigation is rough and mountainous, the level areas being confined to narrow river valleys and a few small plateaus.

Most of the dykes worked at the present time are well up on the mountain sides and in some cases such dykes have been found in the present crests of mountains. Similar deposits are found, however, as low as the level of the present river beds and are apparently no more advanced as regards kaolinization than are the deposits located at higher levels.

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In every case studied the dyke is intruded into a micaceous gneiss, best known as the Carolina gneiss. This gneiss seems to have withstood weathering to about the same degree as the intruded material, the walling in every case studied being disintegrated when kaolinization has occurred and to about the same degree.

The pegmatite of these dykes consists of feldspar and quartz in more or less intimate mixture, varying from a fine granite to associated masses of pure feldspar and quartz. In no case, however, have either been found alone and the ratio of quartz to feldspar seems reasonably constant. In the mixture is found mica (both as muscovite and biotite), garnet, beryl, tourmaline and small quantities of other secondary minerals.

The structure of the dykes is peculiar and leads one to believe that they may be a series of intrusions.

The structure of these dykes is graphically shown in the accompanying sketch, Fig. 1.

The material adjoining the hanging wall is nearly always quartz in a distinct band. This quartz band may be only a few inches or may be several feet thick. Next to this quartz we generally find a feldspar-rich pegmatite or a narrow layer of feldspar-lean pegmatite carrying garnet, tourmaline and other minerals. Adjoining this pegmatite we will find the massive feldspar if such a stratum occurs in the dyke. Adjoining the massive feldspars, if such occurs, we may expect to find a narrow band of massive isolated lenses of quartz. Adjoining this we find two or more distinct bands of pegmatite, each band being distinct as regards size of grain and percentage of quartz content and impurity. Generally these are next to the quartz band which joins the wall. Between the last pegmatite band and the flint band we may find the mica, although it is not uncommon to find it between the feldspar and the first-mentioned pegmatite. In fact the mica is rarely found continuously between any given bands; and although its general position rarely changes from one wall to the other, its irregularity makes mica-mining a very unsatisfactory business.

Oxide of iron occurs as a stain in infiltrated surface clay and is often so securely set in the crevices of ruptured strata

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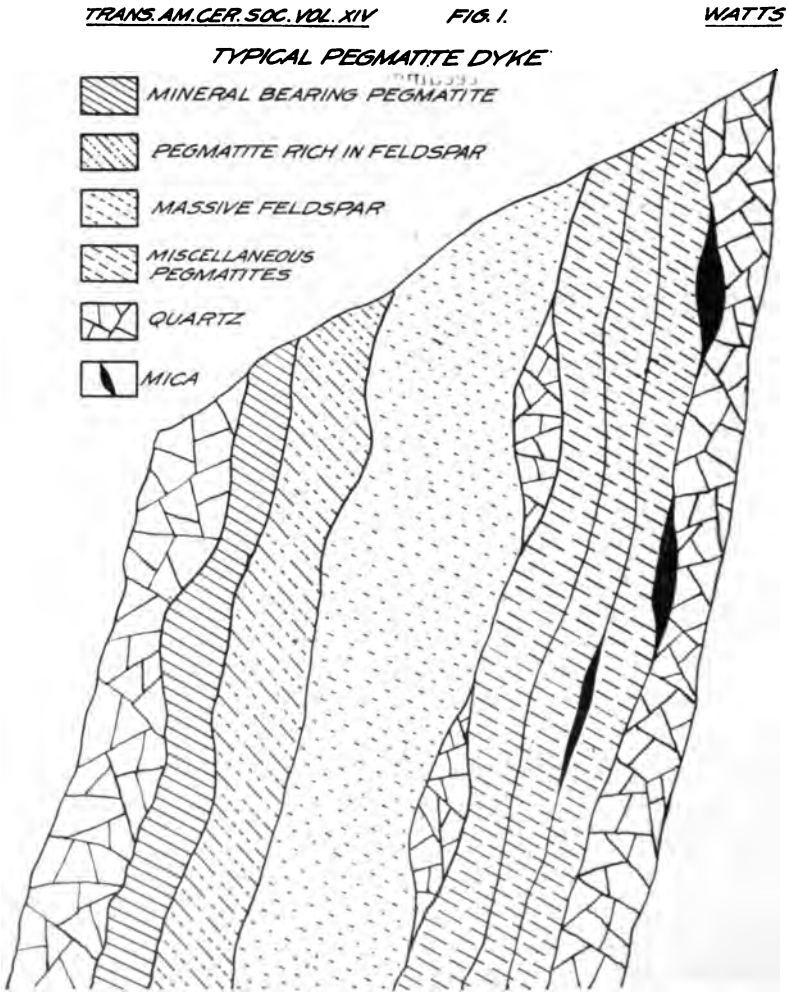

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that no amount of washing will remove it. Fortunately, it seldom penetrates more than a few yards. Where the dyke has kaolinized to any extent we find pockets of iron-stained sand and enclosed lenses of iron-bearing micaceous gneiss which is altered to the same extent as the pegmatite and must be removed with great care, as it is exceedingly friable and its finely divided iron oxide content has enormous coloring power.

Garnets are rarely found as the sole impurity in pegmatite. Where they occur we generally find mica either as muscovite or biotite, or both, and often beryl and tourmaline. Garnets rarely occur in the feldspar-rich strata but are more often found in strata which are made up of quartz and micas. Many dykes which are rather low in feldspar would present industrial possibilities were it not for the iron garnets and fine biotite mica which they carry. Beryl, on the other hand, is found almost entirely in those strata high in feldspar and low in quartz. Tourmaline, like beryl, is found oftenest in the feldspar-rich strata. Manganese and cobalt as earthy oxides are found associated with most of the dykes studied. These generally occur as wad or as asbolite.

The quartz band, which adjoins the hanging or foot wall in most of the dykes, is ruptured apparently from cooling strains, and in the crevices thus formed we may find the deposits of wad or asbolite above referred to. They exist as brown or black powdery material loosely filling the crevices or as nodules adhering to the quartz. Only in two instances have either of these materials been found intermixed with feldspar or kaolin. At one point in Macon Co., N. C., a few nodules of asbolite were found in the kaolin bed; and in the Isinglass Hill kaolin deposit these nodules are very common indeed.

Cassiderite (oxide of tin) is found associated with a kaolinized pegmatite dyke at Lincolnton, Lincoln Co., N. C. This deposit, however, lies outside the district directly under investigation as does also the Isinglass Hill deposit, both being south of the Blue Ridge Mountains. However, their occurrence and structure are so similar to the deposits being studied that it seems permissible to mention them here.

With the exception of the cassiderite and the wad or asbolite

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in nodule form disseminated throughout the dyke, the minerals above mentioned are common to every pegmatite dyke studied; and the problem of their removal or utilization confronts every present or prospective operator.

KAOLINIZATION.

The term "kaolinization" is used to signify the process of decomposition of feldspars and the recombination of a portion of the decomposition products forming kaolin. The process may be considered as follows:

	Molecular combination				Combination by weight			
	K_2O	Al_2O_3	SiO_2	H_2O	K_2O	Al_2O_3	SiO_2	H_2O
Feldspar	1	1	6		17	18.4	64.6	..
Loss by H_2O solution	1				17	..	..	..
Insoluble decomposition products		1	6			18.4	64.6	..
Recombination as kaolin with absorption of combined H_2O		1	2	2		18.4	21.6	6.44
Uncombined or free SiO_2			4				43.0	

We thus see that of 100 parts potash feldspar decomposed we lose 17 parts potash by solution and we have 43 parts free flint and 46.44 parts kaolin, which latter is made up of 40 parts obtained from the feldspar plus 6.44 parts water of combination absorbed. The total of the insoluble products is 89.44 per cent. of the feldspar decomposed. A bed of residual kaolinized feldspar (minus the potash and plus the water of combination in the kaolin formed) should therefore contain 51.81 per cent. kaolin and 48.19 per cent. free quartz.

This is assuming that the deposit is pure feldspar. In nature this is rarely the case. In the present investigation of pegmatites the feldspars are mixed with greater or less amounts of quartz. Other minerals are also present in small quantities so that if we find a kaolinized dyke averaging 40 per cent. pure kaolin we have an exceptional case.

It rarely occurs that the kaolin and quartz products of the feldspar disintegration remain evenly distributed throughout the deposit. The tendency seems to be for the kaolin to filter its way down through the quartz particles until it has formed

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a compact mass, where it packs together into a bed which sometimes runs 92 to 93 per cent. kaolin. Below this bed in the dyke we find another strata of quartz sand which with depth becomes richer in kaolin until another bed of nearly pure kaolin is encountered.

The extent to which this process has gone on varies in different dykes and different localities, but it is more or less apparent in every dyke studied.

As the extent to which kaolinization has progressed varies inversely with the depth, it is not surprising to note that the kaolin decreases in plasticity with the depth of the dyke below water level until the proportion of semi-kaolinized material becomes so great that deeper mining for kaolin is impractical. This semi-kaolinized material, if devoid of plasticity, acts like feldspar or quartz sand in the washing process and may all be removed by the mica troughs and screens.

The depth at which this unplastic material becomes apparent in the dykes studied can be roughly set down at 40 to 45 feet, although the richest and apparently most plastic kaolin is always encountered when the present water level is reached. It is doubtful if this kaolin is really more plastic than the rich portions encountered at high levels but it appears so, owing to the excess of water which it carries. In some dykes the kaolin content steadily increases until the water line is reached, and in such cases the deposit at that point is very rich indeed. These dykes exist in all stages of decomposition from fresh feldspar to perfect kaolin. The topographical location seems to be no guide in determining the extent to which kaolinization has progressed. Fresh feldspar and completely kaolinized feldspar lay almost side by side and at the same elevation. On Tremont Mountain, Macon Co., N. C., we find fresh feldspar and kaolin deposits only a few hundred feet apart on the same level. The two deposits are identical in structure, each having narrow veins of mica-bearing pegmatite along both walls, and a horse of pure quartz cutting the dyke through the center vertically. At Penland, Mitchell Co., N. C., a deposit in an advanced state of kaolinization is being worked for kaolin, while fifty yards distant a fresh feldspar dyke is being worked. In this case, however,

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the kaolin deposit is not so well defined and appears to have been disturbed by a slide. The feldspar deposit is a well defined dyke. Near Jasper, Pickens Co., Ga., we find a kaolinized dyke following the crest of a low ridge while one hundred yards distant and at a level of fifty feet lower we find a fresh feldspar dyke.

Many other similarly associated dykes of feldspar and kaolin will be found recorded in the description of deposits included in the investigation of this district.

PROSPECTING FOR KAOLIN.

Within the area studied very little prospecting has been done aside from the "ground-hog" mica mining which has resulted from exposure of mica-bearing ledges on the surface.

Dyke formations are so uncertain that only by the most thorough prospecting can the extent of a deposit be ascertained.

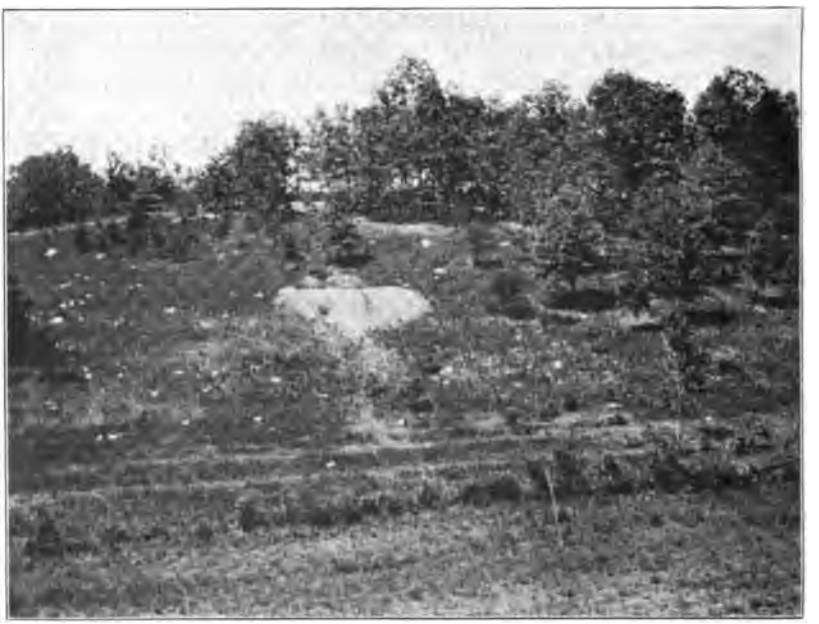

Fig. 2.—Typical surface indications of a disintegrated pegmatite dyke, Macon Co., North Carolina. The white quartz boulders, which once constituted a band in the dyke and which alone have withstood disintegration, are scattered about over the belt beneath which we may expect to find kaolin.

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The surface indications are mainly confined to scattered quartz boulders except where a wash may expose kaolin or pegmatite in dyke structure. A typical surface indication is shown in the accompanying photo (Fig. 2).

MINING AND REFINING THE KAOLIN.

Open-cut mining is employed exclusively on but one property in the district. At the Hewitt Mine in Swain Co., N. C., shown in

Fig. 3.—Open-cut mining of kaolin. Frank R. Hewitt operations, near Almond, Swain Co., North Carolina. The quartz band is absent from this dyke, and the low kaolin content indicates a somewhat different structure from that of a majority of the dykes of this district.

Fig. 3, the overburden is removed by scrapers until that portion is removed which overlays the dyke to the depth which is

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kaolinized. A vertical cut is made through the hanging wall and the slope of the foot wall is followed, making a V-shaped opening. The walling is so friable, however, that this method causes much trouble from slides, as shown in the illustration; and other operators have resorted to open-cut methods only so far as the walls will stand safely, which is a maximum of about thirty feet. Below this depth the circular shaft and tunnel system is employed in every case.

The combination of these two methods is shown in the illustration of the Franklin Kaolin and Mica Co. operations in

Fig. 4.—Combination open-cut and shaft mining. Franklin Kaolin and Mica Co., Iotla Bridge, Little Tennessee River, 4 miles north of Franklin, Macon Co., North Carolina. The quartz band on the right forms the foot wall while the other quartz band bisects the dyke.

Macon Co., N. C., see Fig. 4. Note on the right the quartz stratum adjoining the hanging wall and another quartz stratum cutting the dyke in the center.

The open-cut as a method for removing the upper portions

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of the dyke is well shown in Fig. 5, illustrating the Harris Clay Co. operations at Brysen, Swain Co., N. C. The portion of the working here shown has been worked out as thoroughly as possible without too great expense for removing the enormous overburden shown on the left side of the cut. The outline of some of the circular shafts can still be seen in the foreground.

This dyke was being worked last summer at a point one-half mile farther north, but is rapidly pinching out. This portion of the dyke is shown in Fig. 6 and shows very well the method of open-cutting. Note that the material is removed in two benches and conveyed in dump cars to an incline by which it is conveyed to a point about two hundred feet lower on the mountainside, where a sluice system begins by which the material is floated one-half mile to the washing house. The horse-drawn carts are used only for removing refuse and overburden.

The incline system referred to is shown in Fig. 7. Note in the upper portion of this picture the face of the workings along the mountainside. The present workings are to the right of the head of this incline. The water supply for the sluice is conveyed by troughs which you will note coming from the center right of the picture.

Another good illustration of open-cutting preliminary to shafting is Fig. 8, illustrating the Harris Clay Co. operations at Sprucepine, Mitchell Co., N. C. In the center foreground is a great mica-gneiss lens which was found in the heart of the deposit and which has been carefully worked around and left standing. This deposit is an example of the expanded lens referred to and is kaolinized only about forty feet deep, so that the shafts are rarely more than twenty feet. Two shafts are being operated here, but both are hidden by the obstruction in the foreground. The sluice system for removing the kaolin to the washing plant is carried directly to the mouth of the shafts in these workings and will be noted in the lower right-hand corners of the illustration. This sluice system is merely a trough either V- or U-shaped, into which water is run, and at a lower point the crude kaolin is shoveled in and thus is floated to the washing point. A long sluice system is found very advantageous as it aids in disintegrating the hard lumps.

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Fig. 5.—Abandoned operations of the Harris Clay Co., two miles north of Brysen, Swain Co., North Carolina. Open-cut and shaft mining were combined in working this dyke. The dyke dipped toward the hill, and mining was discontinued on account of the great cost of handling overburden. Note the outline of shafts in the foreground.

Fig. 6.—Present operations of the Harris Clay Co., at Brysen, Swain Co., North Carolina. Open-cut mining preliminary to shafting. This deposit is in the face of a mountain and at an elevation of about 1000 ft. above the washing plant.

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Fig. 7.—Gravity system of handling crude kaolin from the mines to the head of the flume. Harris Clay Co., Brysen, Swain Co., North Carolina. The mining operations, following the face of the mountain, are shown in the upper portion of the view. The flume enters from the left center of the view.

Fig. 8.—Kaolin mining operations of Harris Clay Co., Sprucepine, Mitchell Co., North Carolina. Open-cut preparatory to shafting. Roan gneiss lens found in the center of the dyke stands undisturbed in the foreground. Flume system of conveying crude kaolin to the washing plant is carried to the point of mining operations and may be seen in the lower right and lower left of the view. Note the thin overburden.

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Fig. 9.—Original kaolin mining operation of Gurney Clay Co., 4 miles north of Franklin, Macon Co., North Carolina. Shaft mining exclusively. Note the gradual rise of this knoll. An old horse-drawn whim, now abandoned, lies in the center foreground while a new horse-driven hoist is being operated in the lower left corner of the view.

Fig. 10.—Horse-driven hoist for removing kaolin from shafts. Gurney Clay Co., Macon Co., North Carolina.

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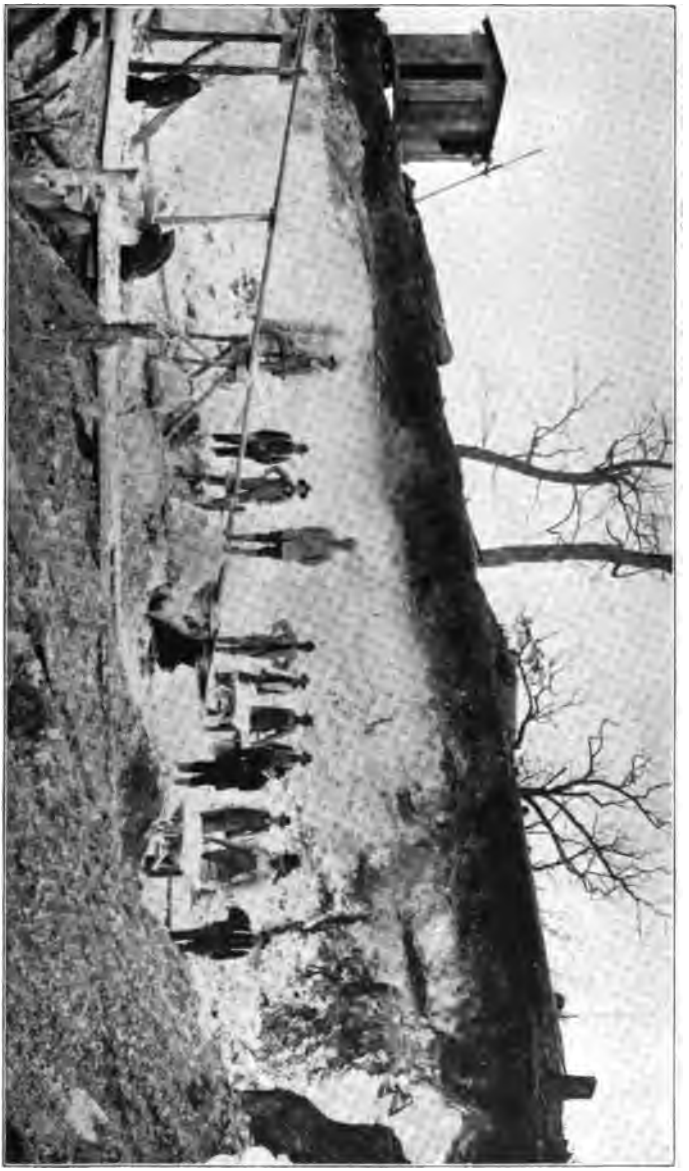

Fig. 11.—Open-cut kaolin mining prior to shafting. Gurney Clay Co., 4 miles north of Franklin, Macon Co., North Carolina. Note the thin overburden, also the numerous quartz boulders scattered about. In the upper right corner stands the stump of a tree along the roots of which the surface water has filtered into the deposit, causing a discoloration at that point.

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Fig. 12.—Shaft mining for kaolin supplementing open-cut mining. Gurney Clay Co., Macon Co., North Carolina.

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Another property where this system of mining is employed is the Gurney Clay Co. operations, north of Franklin, Macon Co., N. C. This deposit is an expanded lens, but of especial richness. Fig. 9 shows this property as originally operated before the open-cut system was introduced. Horse-driven hoists are used to elevate the material from the mines. An old horse-drum hoist, now abandoned, is seen in the foreground. Fig. 10 is a nearer view of the horse-driven hoist. Since these photos were taken the shaft system has been supplemented by an open-cut system by which about twenty feet of the top of the dyke are removed. This is shown in Fig. 11, which is taken looking directly into the face of the hill and shows the remarkable thin overburden at this point. On the right is seen a stained area which occurs in the deposit and which is caused by iron-stained surface clay filtering in along the roots of the tree of which you can see the stump remaining. From a point directly above this stained area another view was taken looking out over the area already mined over. This is shown in Fig. 12, and shows the system of shaft mining which follows up the open-cut system and by which the lower portions of the dyke are removed.

At the mines of the Southern Clay Co. at Franklin, Macon Co., N. C., the shaft system is employed exclusively. Fig. 13 shows the district known as No. 4 mines. The dyke here is about eighteen feet wide and runs east and west across a ridge. The shafts are sunk to about one hundred and ten feet depth, when water is encountered in great quantity, and the dyke shows decreased alteration, making mining for kaolin unpractical. The flume for conveying the kaolin to the washing plant is to be seen running from left to right in this view. The material from these shafts is elevated by means of electrically driven hoists. A good idea of the method of timbering these shafts to prevent caving is obtained from a study of Fig. 14. The timbers are cut in 3 ft. lengths and are 4×6 inch yellow pine or oak. The ends are cut to key the desired circle so that when in place they form a solid circumference which becomes only tighter as pressure is applied from the walling. The shaft is sunk in 3 ft. benches, and the timbering above is retained in place, when the supporting material is removed, by short posts, although the pres-

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Fig. 13.—Shaft mining for kaolin. Operations at No. 4 mines of Southern Clay Co., Franklin, Macon Co., North Carolina. The flume for conveying crude kaolin to the washing plant runs from left to right across this view.

Fig. 14.—Kaolin shaft showing construction of cribbing. Southern Clay Co., Franklin, North Carolina. This shaft being on a hillside necessitates the cribbing extending higher on one side than the other, thus exposing the ends of some of the timbers.

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sure created by the walling is generally sufficient to prevent the timbers moving. The dip of the dyke necessitates a vertical shaft extending into the walling on either one or both sides, and the maintenance of the shaft in circular form necessitates the removal of much worthless material. The dip of the vein is shown in Fig. 15.

Fig. 15.—View in a kaolin shaft showing the dip of the dyke and the great contrast between the white kaolin and the dark red decomposed Carolina gneiss, which forms the country rock through most of the section studied.

When the shaft has reached the maximum depth at which the kaolin content will justify mining, a series of tunnels are run off and the kaolin removed from that portion of the dyke not enclosed within the shafts, which are generally sunk on about forty feet centers. This means tunneling 10 ft. from each shaft if the shafts are 20 ft. in diameter. When the dyke at a given level has been robbed, the tunnels are filled up with material from the surface which has been dumped into the shaft, and thus the shaft filled up until the next higher bench is reached, when the enclosing timbering is removed and that bench robbed as was done on the lower level. The shafts are thus filled before leaving and the overburden, removed in preparation for new shafts, is disposed of. The removal of quartz strata encountered

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in the center of a dyke, and almost invariably along the hanging wall, is a very expensive operation and attended with some danger, owing to the advanced state of decomposition of the associated materials.

The removal of water from the shafts is, however, the most expensive and annoying proposition met with in kaolin mining in this section. The amount of water draining into a shaft will often necessitate a continuous operation of hoisting by means of barrels in order to enable the miners to work. This water is seldom encountered until more than 40 ft. depth is reached, and in many of the older operations mining was abandoned when the flow of water was so great as to demand bailing. In the district studied, the cutting of a tunnel at or below the level where water is encountered has never been successful, although in Lincoln Co., N. C., where a similar dyke is worked for cassiderite, a shaft has been sunk and tunnels radiated from it, and thus a great area has been successfully drained. Another evidence that such a system would be successful is the fact that where two or more shafts are being worked on the same dyke, the deepest shaft is

Fig. 16. Kaolin washing plant of Harris Clay Co., Hog Rock deposit, near Webster, Jackson Co., North Carolina. This operation is the oldest in the district, having been worked continuously since 1890.

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generally troubled with nearly all the water, while the other shafts are comparatively dry.

From the shafts or open cut the crude kaolin goes by sluice to the washing plant, an example of which is seen in Fig. 16. The first process to which it is subjected is known as washing and the machine used is called a washer. This is really merely a process of disintegrating or washing the kaolin free from the mica and quartz particles with which it is intimately mixed in the deposit. The machine is more plainly seen in Fig. 17, and consists of an oblong box with a horizontal revolving shaft through the center. To this shaft arms are attached which stir the kaolin into a finely divided slip. From the washer the kaolin-charged water passes to the sand wheels, which are shown in connection with the washers in Fig. 18. These sand wheels are merely wheels with scoop buckets attached to the radiating spokes, and these scoops scrape the sand from the bottom of the machine and in rising allow the kaolin and water to drain off before the scoop reaches an elevation which will permit of the sand dropping off the scoop. The back of the scoop is sloped toward the outside of the machine so that when the sand slides out it is projected at a 45° angle from the scoop and falls out-

Fig. 17.—Kaolin washer and sand wheels. End view, showing power connection by pulley with the washer and by gear with the two sand wheels.

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Fig. 18.—Kaolin washer and sand wheels (side view). Franklin Kaolin and Mica Co., Iotla Bridge, Macon Co., North Carolina. The refuse from the sand wheels lies in a heap in the left foreground.

Fig. 19.—Kaolin washing plant, including washer and sand wheel shown in Fig. 17. Mica troughs in left foreground. Top frame of settling tanks shown in right foreground. Franklin Kaolin and Mica Co., Iotla Bridge, Macon Co., North Carolina.

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side the machine. In some plants a small jet of water is impinged upon the scoops when they reach the desired elevation and thus the sand is more readily dislodged. Most plants find that at least two batteries consisting of a washer and sand wheel each are necessary. From the sand wheel the crude kaolin floats through a sand box which is of no standard size but is merely a tray-like box where the force of flow created by the washer and sand wheel is overcome by increased surface, and the sand which has not already been removed can be allowed to settle. The outlet of this sand box should be so placed that the water current must turn at least at right angles and a 180° turn is preferable.

From the sand box the crude kaolin floats into the mica troughs. These are shown in Fig. 19. The construction of the mica trough is a matter of much importance in kaolin refining and is very poorly understood. In some plants the troughs are sloped from end to end, and a drop of from one to one and a half inches is provided in each fifty foot length of trough. Thus in a series of eight troughs a drop of eight to twelve inches occurs in four hundred feet flow. In other plants the individual troughs are level from end to end, but each succeeding trough is set one to one and a half inches lower than the one above. This encourages the settling of sand and also provides the necessary drop to maintain flow. The length of trough regulates the degree of separation accomplished, provided too much drop is not introduced; and except as regards the elimination of very fine mica, this means of separation is very efficient.

Another system of mica troughs employed in England but not used, to my knowledge, in the United States is the "fan system" shown in my article of last year on "Kaolin Mining in Europe." By this system the rate of flow and resultant settling of mica is accomplished by conducting the crude kaolin slip from one central trough into a battery of radiating troughs, and the increased area over which the slip is distributed furnishes the retarding force which causes the sand and mica to settle.

From the mica troughs the slip goes to the screen for the elimination of any particles of mica which may have floated to that point. Experience indicates that if sufficient mica trough

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length is provided to eliminate the last traces of mica without the use of a screen, a large amount of slightly plastic kaolin will settle in the last portion of the troughs, and the product, while more plastic on account of the elimination of these particles, will possess an extreme shrinkage, which is objected to by the tile manufacturers who are at present very large users of the kaolin.

The screens used are of three types, *viz.*, the stationary, the rotary and the vibrating.

The stationary screen is most common in this district and is so well shown in Fig. 20 that little additional explanation is necessary. The system as shown consists of four independent screens. The flow from the mica troughs is so divided that an equal portion is diverted in each screen. The screens are made in three sections each. The overflow from the first runs onto the second and from the second onto the third. The screens are

Fig. 20.—Mica troughs and stationary screens. Note the flow of kaolin slip onto the top screens and the small amount that flows over onto the second and third screens. Harris Clay Co. operations, Sprucepine, Mitchell Co., North Carolina.

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so slanted that the excess material flows off readily, thus preventing clogging; and the third screen rarely has any water on it except when the slip becomes too thick and an excess of fine sand and mica is conveyed to the end of the mica troughs.

The rotary screen is known to every one and may be seen in nearly any clay working machinery catalogue. It is very efficient when used in clay working and has this advantage in clay washing over the vibrating screen, that the screen surface is inverted each time the screen revolves, thus loosening any fine mica particles which lodge in the meshes. This is much aided by playing a fine jet of water directly over the screen.

The vibrating screen has been found uneconomical in this district, mainly owing to the fact that fine mica particles clog the meshes and are removed only when broken up by contact with other particles, in which case they pass on through, which is exactly the result that the screen is intended to prevent.

From the screen the kaolin slip passes into the settling tanks. Although the kaolins of this district are very low in plasticity they do not lack fineness of grain and the property of remaining in suspension in water. This is undoubtedly due in part to the soluble alkali present. In nearly every plant alum

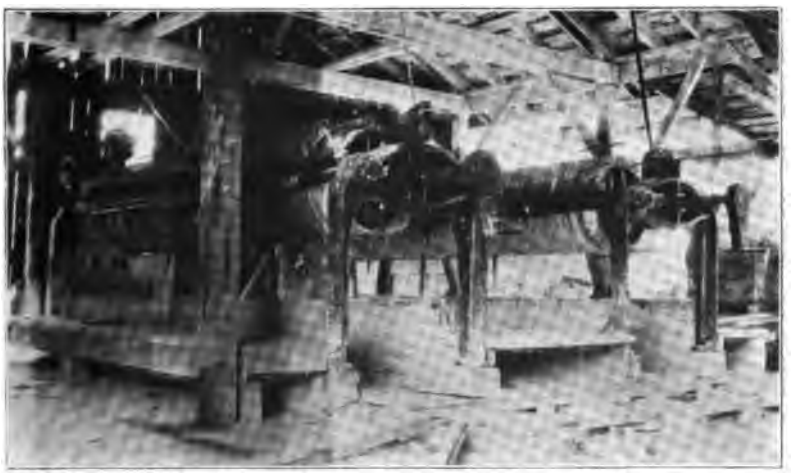

Fig. 21.—Filter presses elevated to permit of use of cars to remove pressed kaolin. Frank R. Hewitt plant, near Almond, Swain Co., North Carolina.

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Fig. 22.—Kaolin washing plant. Flume from mine in center foreground. Mica troughs and settling tanks in left foreground. Double deck dryer and storage bins beyond settling tanks. Gurney Clay Co., four miles north of Franklin, Macon Co., North Carolina.

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Fig. 23.—Kaolin dryer with separate roof which rolls back on a track thus exposing the kaolin to the direct rays of the sun. Harris Clay Co., Sprucepine, Mitchell Co., North Carolina.

Fig. 24.—Ordinary steam dryer for kaolin. Kaolin heaped directly on steam pipes, which are laid along the floor. Harris Clay Co., Sprucepine, North Carolina.

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is employed to overcome the difficulty. This is used in lump form and is introduced in a bag in the trough which conveys the slip from the screens to the settling tanks. From the settling tanks the slip, after removal of the excess water, is transferred to the agitator, where it is thoroughly re-blunged, and then pumped directly into filter presses. The filter presses are elevated to permit of the use of cars for removing the clay, as shown in Fig. 21.

From the presses the clay cakes are taken to the drying house. A number of drying systems are employed in this district. The simplest form of drying is by open-air sheds where the cakes are exposed on shelves and dried by natural evaporation of the water. An improvement and labor-saving arrangement in this district consists in having the open-air dryers elevated and stock bins below (Fig. 22). The clay, when dry, is dumped off the racks through openings in the floor into these stock bins. Another improvement to open-air dryers is shown in Fig. 23. This consists in having the roof constructed to roll on a set of tracks, permitting of its removal from above the clay rocks so that the clay can be dried by direct rays of the sun.

An artificial drying system is shown in Fig. 24. This consists of an ordinary shed, the floor of which is covered with steam pipes. The clay is heaped directly upon these pipes and drying is very rapid and economical. Great care must be exercised not to remove the covering of clay from these pipes in case the heat is shut off, for the pipes will then rust very quickly and stain the clay. The most modern drying system in the district is employed by the Southern Clay Co., at Franklin, N. C. This firm has installed two fan system, hot air, tunnel dryers similar to those employed for drying bricks. The clay cakes are taken from the presses onto cars; and these cars are run into one end of the dryers and come out at the other end, dry and ready for shipment.

SPECIAL PROBLEMS CONFRONTING THE KAOLIN REFINER IN THIS DISTRICT.

The danger of contamination by iron-bearing minerals associated in the dykes and by the enclosing gneisses cannot be too strongly emphasized. The grade of the product can be more

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easily reduced by admission of such material than in any other way. The existence of these kaolins in narrow dyke formations instead of vast beds increases the temptation to mine out every particle of salable material, and this leads operators to accept small amounts of stained material which in more extensive deposits would be rejected.

If the high-grade product which is possible from these dykes in to be produced, it is imperative that no stained material shall be removed simultaneously with the associated kaolin. When iron-stained sand pockets or streaks of iron-stained clay, due to infiltrated water, are encountered, they should be carefully removed and all traces cleaned away before touching the white clay on the same bench, or they should be carefully worked about and all white clay removed from the bench before the stained sand or clay is disturbed. Of course this does not make for cheap operation, but only by such precautions can the danger of contamination be avoided and a uniformly high-grade kaolin obtained, such as the district is capable of producing.

Aside from the variation in the color of the kaolin due to associated materials, the most serious consideration is the variation due to degree of kaolinization. This does not affect the color but affects the refractory value, the plasticity and especially the shrinkage of the kaolins. The influence of degree of kaolinization upon refractory value is shown in Fig. 25, which compares combined water content with refractory value. Combined water content is here taken as an indicator of degree of kaolinization.

Here we see the refractory value increase as the feldspar alters to kaolin and in approximately the same proportion. Many of these deposits are so slightly kaolinized that to the casual observer they are fresh feldspar. An examination, however, shows that the cleavage is becoming notably weak, so that many specimens may be broken with the hands. A determination shows a small amount of combined water and a proportionate increase in deformation temperature. The exposure of these deposits to surface drainage or wash removes the kaolin formed, leaving a mixture of feldspar and quartz, which naturally does not check with this curve, hence only samples from well protected deposits have been considered. The presence of the requi-

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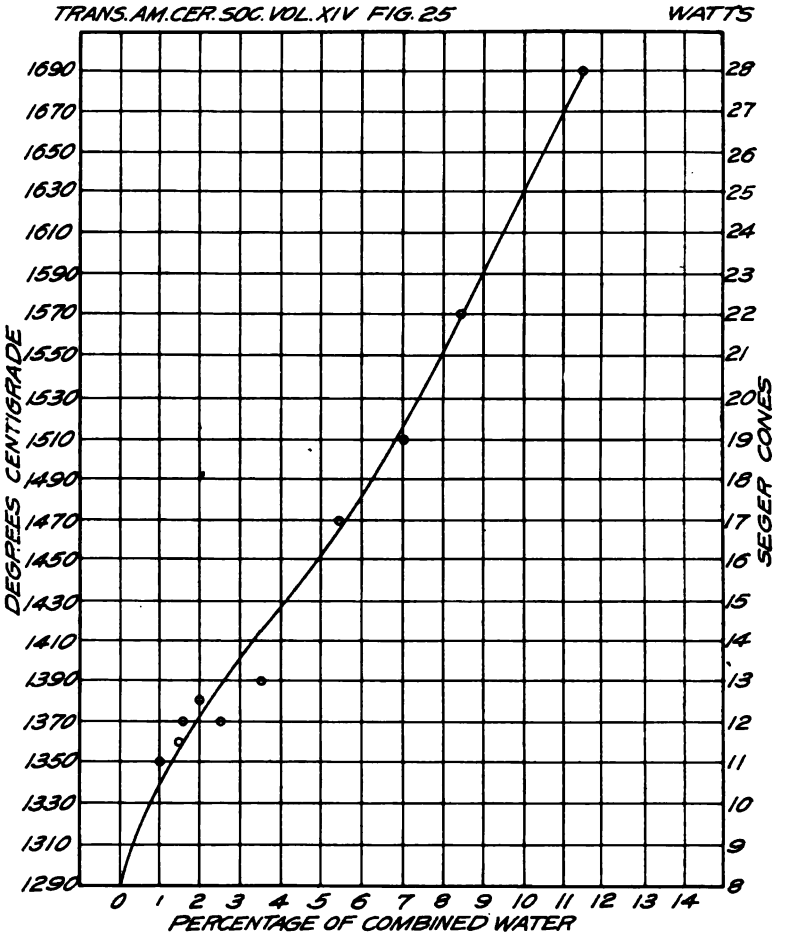

SEMI-KAOLINIZED FELDSPAR
DEFORMATION TEMPERATURE VS. COMBINED WATER CONTENT

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site 13.9 per cent. of combined water cannot be taken as an indication of the development of plasticity. In fact, none of the materials classified in this investigation as semi-kaolinized feldspar possess any real plasticity, nor do they possess sufficient bonding power to permit of their being pressed into shape for test without the employment of some organic bonding agent.

Shrinkage tests made at 1330° C. indicate that the materials containing less than 3 per cent. of combined water deform and hence cannot be measured. A specimen containing 3.7 per cent. combined water shrinks 15 per cent. and is vitreous and translucent, but not deformed. A specimen containing 5.5 per cent. combined water (*i. e.*, 40 per cent. kaolinite) shrinks 7.5 per cent. and is semi-vitreous but not translucent. Those specimens possessing more than 5.5 per cent. combined water are not vitreous at this temperature but show increased shrinkage with increased content of combined water. A specimen containing 11.3 per cent. combined water shows a shrinkage of 15.25 per cent.

This variation in shrinkage is due to two causes. In the slightly kaolinized specimens the shrinkage includes that of vitrification, while in the specimens nearing complete kaolinization the high shrinkage is due to the high combined water content and the fine state of subdivision of the kaolin particles.

The presence of this semi-kaolinized material with its variable shrinkage is very probably the cause of much of the shrinkage variation noted in the washed kaolin from this district.

A study was made of the variation of physical properties with depth in a number of especially well exposed deposits. Samples were taken from a point near the surface, and other samples were taken from the lowest practical mining level. The accompanying table shows the combined water content, the proportion of the various sized grains in the samples taken, and the shrinkage at the various stages of manufacture.

We see by a study of this table that a variation in shrinkage exists in all of these deposits but with no regularity. The variation between the different deposits is far greater than between the different depths in any one deposit. This is of course

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assuming that a washing process is employed which will remove all the hard granular feldspathic material.

VARIATION OF PHYSICAL PROPERTIES OF KAOLINS WITH DEPTH OF DEPOSIT.

Deposit	Location in deposit	Combined water content	Per cent. coarser than 100 mesh	Per cent. between 100 and 200 mesh	Material finer than 200 mesh		
					Shrinkage wet to 110° C.	Shrinkage 110° C. to 1330° C.	Total shrinkage
K 3	Bottom	14.20%	24.10%	8.14%	3.6%	5.4%	9.0%
K 3	Top	13.00%	6.56%	10.34%	2.8%	6.8%	9.6%
K 9	Bottom	12.64%	22.51%	6.02%	5.0%	6.8%	11.8%
K 9	Top	11.32%	46.80%	7.16%	6.0%	6.4%	12.4%
K 58	Bottom	12.83%	82.53%	5.07%	4.4%	7.4%	11.8%
K 58	Top	11.69%	75.40%	8.29%	3.0%	4.8%	9.8%
K 12	Bottom	10.00%	42.20%	8.08%	4.4%	9.2%	13.6%
K 12	Top	10.33%	21.44%	5.00%	3.6%	5.4%	9.0%
K 82	Bottom	11.26%	29.52%	13.00%	3.6%	7.6%	11.2%
K 82	Top	11.17%	15.30%	5.60%	4.4%	6.0%	10.4%

The production of a uniform product from any given deposit depends therefore upon the ability or willingness of the operator to work all levels in the same proportion, or in a constant ratio to each other. This calls for a storage system at the mines so that excess material from any given level may be reserved until the proportions of materials from other levels will permit of its use. The same result may be accomplished by reduction of output from any level which tends to produce temporarily more than its average amount of material. However, for economy of operation it is advisable to operate at a maximum capacity and the expense of maintaining a reasonable storage of unwashed clay will compare favorably with the added cost due to reduced production, especially if water must be removed from the workings.

The same proposition confronts an operator who attempts to blend materials from two or more dykes. A constant ratio must be maintained between the amounts of material introduced from the different dykes. Owing to the greater difference between dykes than between different levels of the same dyke, such a pro-

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cess of blending demands special attention and care if the product is to be maintained uniform.

Another detail of refining which demands special attention is the amount of material fed into the washing plant as compared to the amount of water flowing through it. This subject is entitled to more careful consideration than it has received up to this time. If the plant is crowded to its capacity, the slip passing through the sand box and mica troughs may have a specific gravity of 1.55 and can thus float much fine mica and grit which it could not carry if only moderately charged with crude kaolin. For satisfactory washing operations in this district a specific gravity of 1.30 to 1 for the crude kaolin slip appears to work most successfully, although this cannot be laid down as a standard for all operations. The main point brought out here is that a slip of uniform density should be fed into the washing plant if a uniform product is to result.

Another precaution which will materially assist in producing a uniform product is the maintenance of ample storage tank capacity for slip, thus enabling the operator to blend his mine products of, at least, several days before pressing.

Another detail worthy of attention in connection with kaolin refining operations is the uniformity of the water used for washing. Usually the source of supply is a spring brook, and this tends to vary with the season due to surface water additions. The soluble salt content varies with variation in flow and season, and this has a marked influence on the capacity of water to hold kaolin in suspension. Where variation in this property exerts so great an influence on the product, the maintenance of a uniform water supply would appear to be a wise investment.

The practice of re-using the water in such operations as kaolin washing should not be attempted except when the supply is limited and the practice is a necessity. The kaolinizing process which the feldspathic matter in the dykes has undergone has, as is explained heretofore, liberated a considerable amount of alkali and doubtless some of this remains associated with the kaolin by adsorption. If water for washing is re-used it soon becomes charged with these soluble salts, and its ability to remove the soluble material from the crude kaolin is lost.

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The kaolin produced from water charged with soluble salts will hence contain considerable soluble salt, and its refractory value be proportionately reduced.

It is advisable, where the re-use of washing water is necessary, to replace at least a portion of this by fresh water from time to time and thus prevent the stock water from becoming too concentrated. The addition of fresh water to replace loss by evaporation does not provide any relief along this line as the total alkali content in that case remains the same since by evaporation no alkali is removed.

The removal of mica and its possible utilization should be carefully considered. Mica is present in varying amount in all the dykes of this district, and its removal is imperative whether it is thereafter made a merchantable article or not. Coarse mica does not present any difficulties to the kaolin miner but can be picked out by hand and sold to considerable profit. The only difficulty arising from the presence of coarse mica is due to carelessness. When it is allowed to enter the flume with the other associated minerals of crude kaolin, it soon becomes battered to pieces and enters the washing plant in such small particles that its removal even by the aid of fine sieves is difficult and often impossible.

All mica in blocks should be removed with the coarse flint particles before the crude kaolin enters the flume. One-fourth to one-eighth inch mica may be removed by the settling troughs but its separation when pulverized is a very difficult problem, and it resolves itself into a problem of removing the mica while coarse and to this end the process of disintegrating the crude kaolin without injuring the mica present. To this end the sluice from mines to washing plant should be of gradual slope and without sudden angle or drops. The spokes in the washers should clear the sides and bottom so that no mica present may be crushed. The scoops on the sand wheels should clear the bottom of that machine sufficiently so that no mica lodging there may be battered to pieces.

Mica finer than one-eighth inch diameter is the most difficult to remove of any impurity in crude kaolin. In successfully removing the other non-plastic material, a certain amount of

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fine mica is of necessity carried past the mica troughs, and a fine screen is necessary for the removal of this mica. A sieve of 100 meshes per lineal inch is customarily used for a stationary screen. If a vibrating or revolving screen is used a sieve of 120 meshes per lineal inch is employed.

The recovery of the fine mica from the sand in the mica troughs and from the slime on the screens should be considered very seriously as the material thus obtained, if separated from the associated sand, should make a product suitable for use in the manufacture of lubrication mixtures and in many instances suitable for use in the decoration of wall paper.

A process for the recovery of this fine mica would consist of a separation based on size of grain. The mica particles, being in plates while the quartz and other associated materials approach spheres in shape, would permit of a separation by currents of water. Such apparatus is not at present on the market but could be easily constructed to remove the quartz by hydraulic methods. The biotite, chlorite and vermiculites, being much more friable than the muscovite, are naturally broken into finer particles and may be removed without difficulty, provided enough water is furnished to enable the coarser particles to settle without interference.

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AN APPARATUS FOR THE DETERMINATION OF THE EXPANSION COEFFICIENT OF SOLID BODIES.

By P. A. Boeck, Worcester, Mass.

In the course of some experimental work and investigation of certain phenomena in the manufacture of grinding wheels by the vitrified process, about three years ago, it was found necessary to determine the coefficient of expansion of bodies for which no data were available.

On investigating the various types of apparatus used it was found that none answered all of the requirements, the principal difficulty being in the use of large, and in some cases complicated, test pieces on which the determination was made. As the main line of work was to be on abrasive materials having a hardness of 9 or more in Moh's scale and infusible except at the temperature approaching that of the electric arc, it was manifestly evident that a small test piece of simple shape would be required.

The main considerations in the design of an apparatus for the work in hand were arranged in the following order of their importance.

1. Ease of preparation of sample.
2. Temperatures up to 1000° C. and with certain slight modifications up to the softening point of quartz.
3. Determination of absolute values for the coefficient.
4. Reasonable accuracy.
5. Rapidity and facility of operation.
6. Adaptability to test pieces of any material.

The principle on which the apparatus, as finally adopted, is based was suggested by an instrument seen in the Reichsanstalt which depends on the compensation in expansion of two concentric fused quartz tubes, the outer one serving as a heating chamber for the test piece and the compensating inner quartz tubes on either side of it. The outer quartz tube is clamped tightly by a support at one end and the inner set at the opposite end, the difference in expansion of the inner and outer sets of tubes due to heat being measured by a micrometer microscope.

The final development and arrangement of apparatus took

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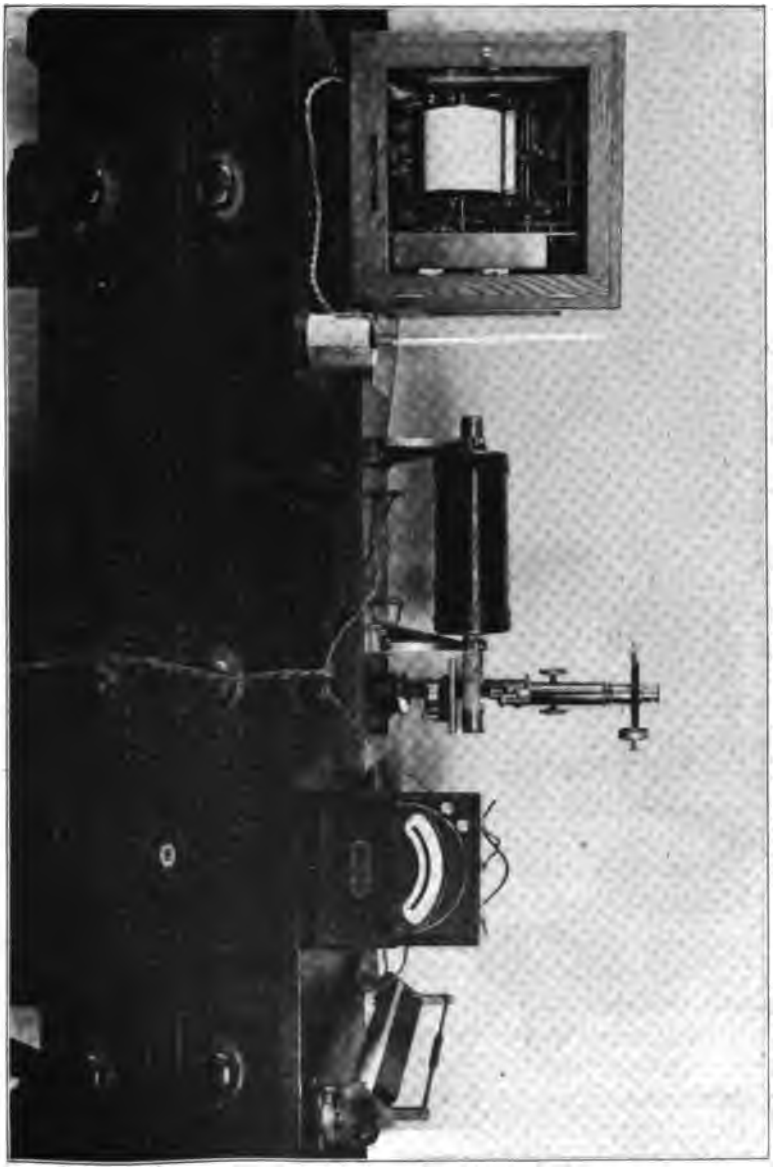

Fig. 1.

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the following form (Fig. 1): An expansion furnace in which the test piece is uniformly heated by means of resistance wire wound about a fused quartz tube, the expansion of the test piece being transmitted to a smaller fused quartz tube concentric with the first and bearing a cross hair upon which is focused a filar micrometer attached to a high power microscope. The movement of the cross hair is observed simultaneously with the temperature of the test piece inside the furnace as is indicated by a thermocouple which is in intimate contact with the test piece. The temperature is measured on a recording millivoltmeter and is corrected for the temperature of cold juncture as indicated by the thermometer in a cold juncture block. The degree and rate of heating of the furnace in which the test piece is placed is gauged by the ammeter and controlled by a carbon compression rheostat in the heating circuit.

The detail of the construction of the expansion furnace is shown in the accompanying elevation which will be described briefly:

A fused quartz tube (Q1) (Fig. 2) 41.3 cm. (16.25 inches) long and 2 cm. (0.78 inch) bore, having tightly affixed brass end pieces, is wound with 6.5 m. (25.5 ft.) of flat "Nichrome" wire (R) 0.36 × 1.1 M.M. (0.014 × 0.045 inch) in section closely covering 15 cm. (6 inches) of the tube slightly to one side of its center and connected to the terminals (T1, T2), as shown. The active portion of the heating element, *i. e.*, the heated portion, is covered by a thin layer of Alundum cement to prevent corrosion and to distribute the heat uniformly. The tube is rigidly fastened by the bronze support at the right side and allowed to slide freely in a similar support on the left so that any expansion that occurs due to the heat will be towards the left.

A fused quartz disc (Q 4) of the diameter of the outer quartz tube, having a hole large enough for the introduction of a thermocouple, presses firmly against the end of the outer tube and prevents any movement of the inner quartz tube (Q 3) towards the left. The test piece (T), which is in the form of a tube 10 cm. (3.937 inches) long and 1.8 cm. (0.709 inch) in diameter, having a hole 1 cm. (0.393 inch) in diameter, is held in place on either side by fused quartz tubes (Q 2, Q 3) which allow of movement only towards the right, all free motion being taken up by

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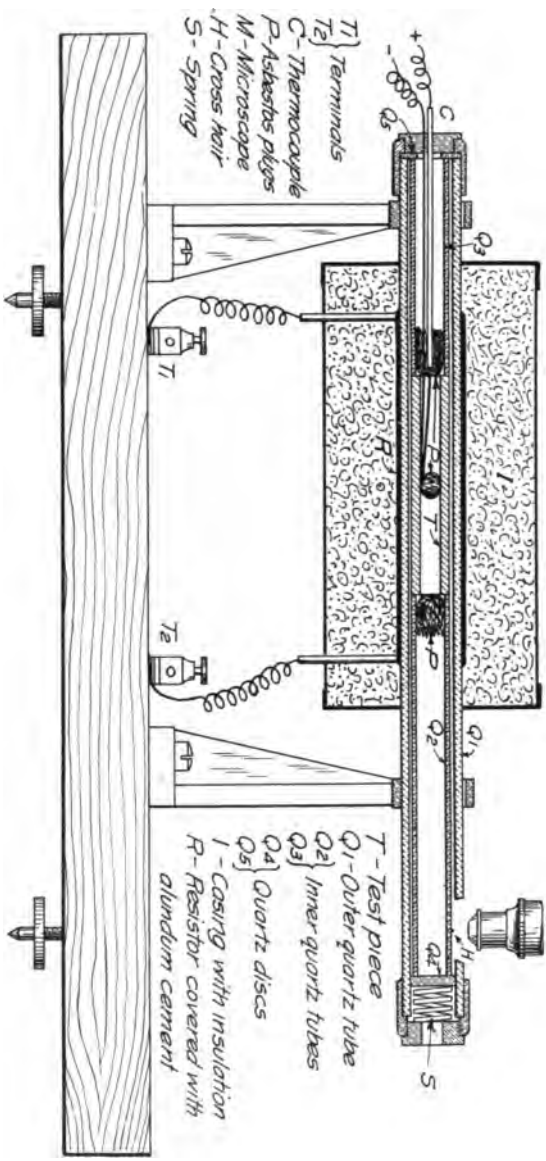

TRANS. AM. CER. SOC. VOL. XIV FIG. 2. M. BOECK

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a helical brass spring (S) of the proper tension placed at the extreme right of the inner tube (Q 3). The inner tube at the right side bears a cross hair (H) of a single strand of black silk, on which the micrometer microscope is focused.

It will be seen from this description that each set of tubes has free movement only in opposite directions, the outer tube capable of moving only toward the left and the inner set only toward the right, which latter movement is diminished, with respect to the cross hair, by the distance the outer tube moves to the left by virtue of its expansion due to its being heated. But the degree to which both inner and outer tubes are heated being the same at any point, the expansion of the quartz tubes will be equal and opposite in direction and will therefore compensate each other, so that the net movement of the cross hair on the inner tube will be due entirely to the expansion of the test piece. If this expansion be divided by the true rise in temperature of the test piece, the linear coefficient of expansion per unit length per degree rise in temperature may be readily obtained by a simple calculation.

There is, however, a slight correction for the expansion of the outer quartz tube about the test piece and for a slight deformation of the fixed standard at the right, due to warming, which is known as the "Correction for the quartz and instrument."

The equipment used for measuring the change in position of the cross hair consists of a Bausch & Lomb microscope fitted with a filar micrometer attachment capable of measuring with the $^2/_3$ inch objective any variation in position of the cross hair to within a possible error of 0.00052 mm. (0.000020 inch). This is calibrated by a standard slide having parallel lines ruled one-tenth and one-hundredth millimeter apart. Not being able at the magnification used to obtain a cross hair sufficiently fine so that no error would be introduced, it was found most advantageous to use a dark dyed single strand of silk and select one particular portion of this to be followed.

The most difficult problem confronted in a determination of this kind where absolute values are sought is the uniform heating and the measurement of the true temperature of the test

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piece. Where high temperatures are used this is by no means an easy matter, but by eliminating one obstacle after another we have been able to reduce the error in this apparatus from this cause to a minimum.

The test piece is supported and prevented from coming in contact with the heating tube by means of two rings of platinum wire placed near either end of the piece, insuring a uniform heating by radiation except at the point at which the actual contact with the platinum occurs, which is so small as to be negligible. The quartz tubes on either side of the test piece are of course supported in like manner.

The next consideration is the placing of the hot juncture of the thermo-couple in the test piece in such a manner that it will record the true average temperature of the test piece as accurately as possible. The form of the piece is such that it will quickly assume the temperature of the surrounding bodies, *i. e.*, the walls were made as thin as is consistent with ease of manufacture, so that by placing the juncture of the couple in close contact with the inner wall of the test piece the proper temperature will be indicated. This is done by placing a plug of pure asbestos fiber beside the couple in the center of the piece.

In winding the resister about the outer quartz tube, a space of 3 cm. (1.18 inches) on either end of the test piece was covered to assure a uniform temperature to the piece and to prevent a lowering of the temperature of the extremities by radiation and conduction losses.

The thermo-couple used was a platinum, platinum-rhodium alloy, made by Wilson and Maeulen, and standardized by the Bureau of Standards. As a precautionary measure the couple was "glowed out" frequently by an electric current and checked by determining the freezing points of standard pure metals. The free ends of the couple were immersed in mercury contacts in a steel cold-juncture block having a thermometer placed to record the temperature of the mercury. The cold-juncture corrections determined by Offahaus and Fischer (Electrochemical and Metallurgical Industry, IV, 9–362) were applied to all readings. The electromotive force of the couple was measured by

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a Taylor "Thread recorder" of high temperature, and amperage was taken simultaneously every minute throughout the entire run.

The remainder of the apparatus requires no further description except the possible explanation that the current (a 110 volt lighting circuit) passing through the heating coil was so gauged that a uniform rise of 20 degrees centigrade per minute was maintained within the test piece.

It is somewhat outside the province of this paper to discuss results obtained; however, some characteristic expansion curves may serve to show the accuracy of the apparatus and be of interest in suggesting new lines of work in this very interesting and important field.

Fig. 3. The expansion curve of "Alundum"—electrically fused alumina used for abrasive purposes. This material is essentially a glass. Note the linear expansion.

Fig. 4. The expansion curve of "Crystolon," a recrystallized piece of silicon carbide, also used for abrasive purposes. The expansion of this material is approximately half that of the "Alundum." Note the position of the cooling or contracting curve showing the small temperature lag and also the fact that the latter curve eventually reaches the initial position, indicating that the expansion and contraction through the rise and fall of the temperature are the same. The coefficient of linear expansion is calculated from the mean expansion as shown by these two curves.

Fig. 5. The expansion curve of a sample of ball clay burned at cone 12. Note the peculiar character of the curve indicating a well marked thermal reaction at a comparatively low temperature. This is also shown more strikingly and checked in the following curve.

Fig. 6. Two expansion curves of a fire clay burned at cone 12. This curve was so unusual that a check run was made. This, in verifying the previous run, shows the capability of the apparatus for obtaining concordant results.

The apparatus is not limited to ceramic or mineral bodies

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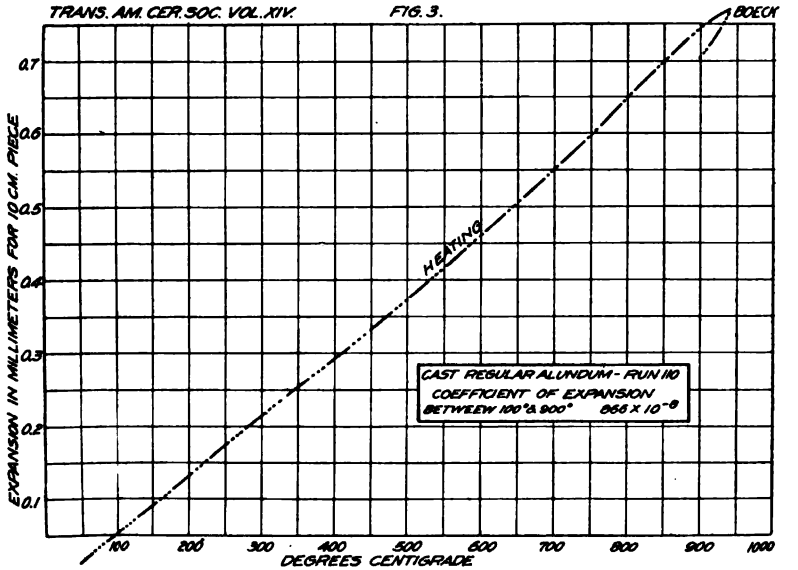

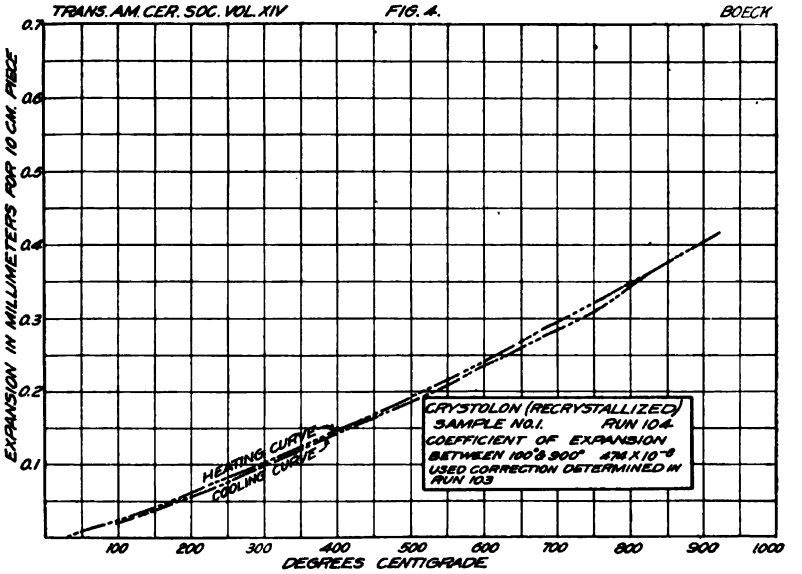

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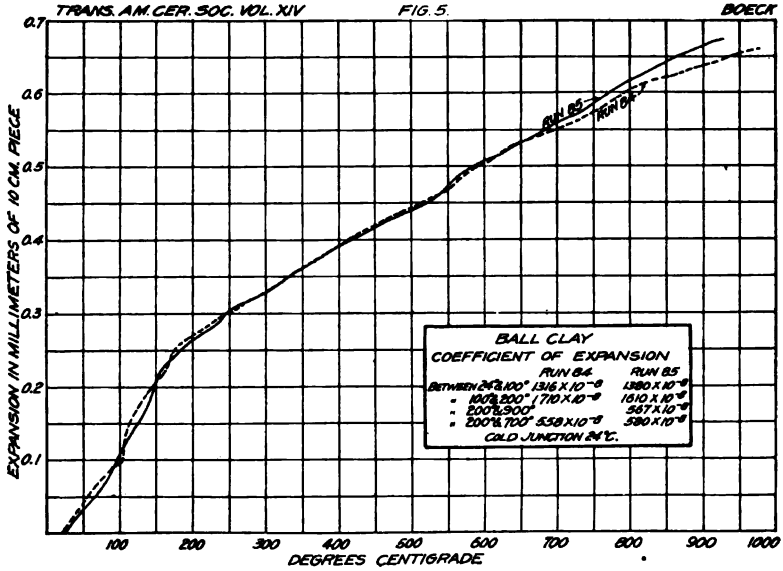

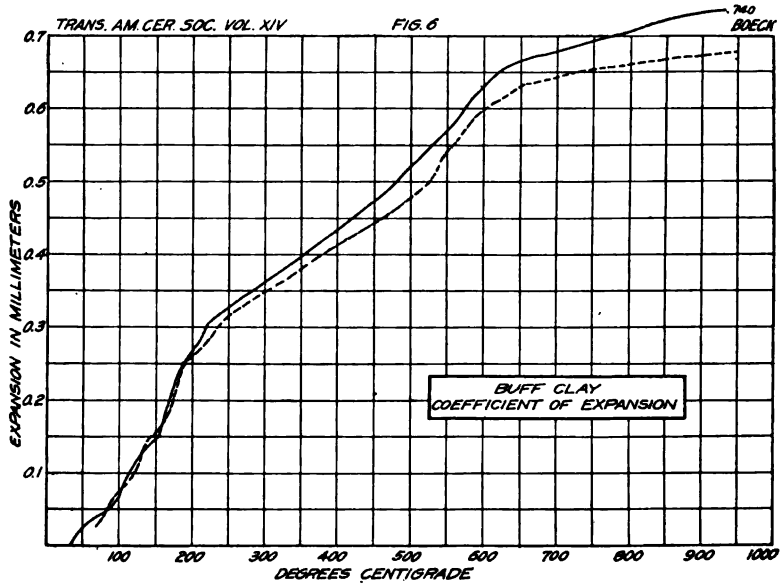

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but is adapted to any material which can be formed into the required test piece. Standard metals have given results which check very closely with the accepted values of their coefficients.

The temperature limit of the apparatus as described is about 1100° centigrade. By using a resistance wire of platinum or iridium the apparatus may be used up to the softening point of quartz.

RESEARCH LABORATORIES,
NORTON COMPANY,
WORCESTER, MASS.

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RECENT DEVELOPMENTS IN THE REFRACTORIES INDUSTRY.

By F. T. HAVARD, Madison, Wisconsin.

HISTORICAL.

Although the art of the potter and the knowledge of the chemist and geologist have combined to develop the ceramic industry, perhaps the combination of these with the skill of the mason has been most effective in urging the progress in the preparation of refractories, which have supplied the sinews of war to the furnace men in the extraordinary changes which have been made in recent years in the science of metallurgy. During the middle ages, the furnace operator was at the same time the worker in clays, a potter of no mean skill, who had considerable intelligence in the selection and application of refractory materials. Agricola describes the methods used in preparing fire clay retorts and crucibles, and the practice in constructing furnaces in the middle ages. The clay was pugged, thrown by hand, dried and burnt in wood fires. The furnaces in his day were similar to many used at the present time in Europe, in which the movable roof, made of nicely fitted tiles to form an arch inside a round angle iron band, superimposed the hearth made of tamped bone ash, marl, silica or some other refractory material.

The use of kaolin to make porcelain also helped the chemist, who gained a lively appreciation of the qualities of the purer clays. His acquaintance with bone ash, carbon, plumbago and wrought iron anteceded that with silica, while he rapidly becomes conversant, through experiment, with the properties of bauxite, magnesia, dolomite and marl. It is only within quite recent time that the use of chromite, steatite, and the various artificial refractories has developed.

Thus the art of the potters preceded that of the brick and refractory makers in Europe. It was not so, however, in America. We read of brickyards on Long Island in 1640, and the industry has continued to develop on a scale larger than and different from that of any other country. Following the use of fire clay, came the application of silicious rocks in natural state such as pudding

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stone, granite and quartzites which were found suitable to withstand the corrosive action of metals and slags at high temperatures. Then bone ash had its day, followed by graphite until a happy combination of ground rock and clay mass led the way to the discovery of the advantages offered by the silica brick material.

Soon after the introduction of aluminous brick, the value of graphite as material for crucibles and furnace linings was realized. It is interesting to note that a patent, No. 767, Jan. 25, 1762, was granted to Wm. White for a "new invention in the manufacture of crucibles for the melting of metals and salts." The specification directs that Stourbridge and Dorsetshire clay are to be mixed with Woolwich sand and water and that the mixture is to be trodden with the feet. The use of coke in admixture with Stourbridge clay in the manufacture of crucibles was patented by Anstey, who used two parts of fine ground clay with one of pounded gas coke, and prescribed that the coke was not to be crushed finer than one-eighth of an inch and that the mixture should be worked with water and well trodden. Anstey's pots withstood eighteen successive fusions of cast iron, provided they were not subjected to frequent and rapid cooling, and earned for him a prize of a silver medal and the sum of twenty guineas for his invention from the Society of Arts. It was not long afterwards that an effort was made to substitute plumbago for coke and in 1828 Mr. Charles Sidney Smith was awarded £20 for the manufacture of crucibles composed of Stourbridge clay, coke and plumbago. The process of making these pots or crucibles is described in Vol. 47 of the Transactions of the Society of Arts. They seem to have been of an even homogeneous character and of considerable strength and refractoriness.

In 1856 Deville made alumina crucibles from a mixture of gelatinous alumina with a proper proportion of calcined alumina and from an intimate mixture of equal parts of alumina and pounded marble. These crucibles when exposed to a high temperature acquired a remarkable degree of solidity and resisted sudden and great changes in temperature. In 1869 bauxite, which had been previously analyzed by Berthier, was suggested

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as a raw material for crucibles. It obtains its name from the hill called "Colline des Baux," from which Berthier obtained his sample. Some bauxite in Andalusia had been used by the Moors for the manufacture of terra cotta ornaments, but it was not until the end of the '60s that it was used as a lining for furnaces. It is not surprising, considering its physical properties, that it has not obtained a wider application for this purpose.

Lime crucibles were made at this time, and experiments were conducted by Deville in applying them for smelting; but on account of the reaction of lime with carbon and its tendency to slag with any silicious or aluminous material it did not obtain a wide field of use. Furthermore, the lime crucibles disintegrate when kept for a long time and are unsuited for the melting of iron or iron ores on account of the tendency to form calcium ferrate. Magnesia, on the other hand, soon obtained wide and favorable reputation as a refractory lining and was used as far back as 1870 in Bessemer converters and open hearths. Since that time it has steadily grown in favor and is perhaps to-day the most favored of all refractories. Hardly less useful than magnesite is dolomite, which has been favored by the English and German iron masters as a lining for open hearth furnaces and Bessemer converters. Unburnt limestone, when mixed with clay, has been used as a lining in more recent years to replace the old-fashioned bone ash and marl, both of which were used in the 18th century, but in turn has given way to magnesite. It is only within recent years that the high-grade magnesite bricks manufactured from Grecian and Styrian deposits have obtained the high reputation they now deservedly enjoy.

RECENT DEVELOPMENTS.

The developments within the past few years have been of a very different kind. Thirty years ago the refractories industry in the United States produced products to the value of $400,000 a year. Now their value is between fifteen and twenty million dollars.

This is altogether due to the progress made in the metallurgical industry. The wealth arising from this industry would have been impossible of realization had it not been for the energy of

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the refractory makers in supplying durable materials to stand severe physical and chemical strain. In 1820 a blast furnace made eighty tons of iron a week, in 1860 about that much per day. Now it makes 500 tons daily. In 1880 a copper furnace would smelt twenty to thirty tons of ore per day; now it handles as much as two thousand. Coke oven, blast furnace and cement kiln developments are only a few of a similar character. The refractories industry has amply proved its ability to cope with these new demands. One firm alone produces over one million refractory brick a day. There are about 400,000 silica and 50,000 magnesia brick produced daily in the country.

It is not only in quantity but also in quality that the refractories industry has met the demands made on it by the enormous furnaces, stoves and ovens. And to its credit, it has generally been first in anticipating these wants and has frequently educated the operators in the requirements of good, modern practice.

Yet no remarkable change has been made in the character of the raw material used, nor yet in the principle of the methods of manufacture. The Americans have improved in a physical sense the refractory products; their good chemical properties were well known nearly a hundred years ago. We still use fire clay brick. We have improved it for some purposes by increasing the alumina percentage to 60 and 70, such as is contained in "Alusil" bricks recommended for rotary cement kilns. But in the preparation of silica, magnesia, chromite, graphite and the artificial refractories we have achieved signal progress.

Unfortunately, as the industry developed there arose a confusion of names applied to the silicious refractories. The name Dinas was first used in the beginning of the 19th century by Mr. Weston Young, who worked the silicious materials in the Dinasfels in Wales into brick with the aid of the underlying cretaceous lime. The Young family kept the process a secret until the middle of the century. During this time another kind of silicious brick was being made by grinding and mixing the gannister rock of Sheffield with clay. The name "Gannister" is still generally applied in England to such silicious material bonded with clay. Germans commenced the manufacture somewhat

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later of the clay-bonded silica brick and called it "German Dinas" and advanced its superior qualities as a competitor with the imported English Dinas. When American industry called for acid furnace linings, bricks and mass of the composition of the English gannister were marketed under the name of "Quartzite;" the word "gannister" was restricted to the second class silicious material, won in sandstone and quartz quarries, which was bonded with clay and used in lining converters. The Americans have never used the term Dinas. The first-class silica brick with lime bond is called silica. It would be an advantage to the industry if the terms were standardized. We might comprehend under "silica," brick with approximately 96 per cent. silica and 2 per cent. lime; under "gannister," a mass with about 80 per cent. silica and 20 per cent. fire clay; under quartzite, brick with between 70 and 80 per cent. silica, and reserve the name "Dinas" to the peculiar brick of principally historic interest made from such formations of silica and lime as those of the Dinasfels. At the present time we have more names than distinctions in silicious materials, since Dinas and silica on the one hand, and gannister, quartzite and German Dinas on the other, comprehend the same meaning.

In the manufacture of silica brick, the leading American refractory brick makers have obtained the best results in the use of sedimentary sandstones and quartzites containing about 97 per cent. silica; these, when ground and tempered with less than 2 per cent. of clay, burn into a brick of uncommon properties. At the present time there are two cheap sources of this raw material (in Wisconsin and Pennsylvania), in both of which the silica averages 97 per cent. and is supplemented by alumina and ferrous and ferric iron. Attempts have been made to use pure quartzite with 99 per cent. silica, but without conspicuous success. It would appear that the impurities when totaling less than 3 per cent. and containing not more than 1 to 1½ per cent. of oxides of iron, strengthened the brick by the formation of incipient slag particles. The lime is necessary to hold the silica together during the processes of moulding, drying and burning; and it probably acts as a fluxing agent at the high temperature of burning, cementing the silica particles together. There is no ap-

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pearance of fluxing in the fracture of the brick, which is dry and homogeneous. The slag particles are, however, only in an incipient stage of formation but are sufficiently active to act as a bond. The physical properties of the rock play an important rôle. Sand may not be used because the particles are round and do not interlock and fail to make a cohesive strong bonded brick. Rock which grinds into splinters, which overlap and interlock, forms a satisfactory brick and is always preferred to a material however pure which is or grinds into a granular condition.

The silica bricks have a wide use in the construction of by-product and bee-hive coke ovens, in open hearth furnaces, in the glass, iron, copper, and melting business. Their physical properties of regular expansion and heat diffusivity have endeared them to modern furnace builders who do not require basic materials.

Not less remarkable has been the progress in the use of magnesia in furnace work. Five years ago no copper converter was lined with any material other than gannister. Ten years ago there were but a few basis-lined, open hearth furnaces.

Magnesia or burnt magnesite has in recent years been replacing the old standard dolomite. Magnesia is generally used in the form of bricks, while burnt dolomite was used as mass. The highly refractory qualities of magnesite were realized as far back as 1870, but effort after effort to use it was frustrated on account of the poor physical properties of the burnt mass and bricks. It is only in the comparatively recent years that we have developed the art of making these burnt bricks firm and sufficiently tenacious to stand pressure when hot. The magnesite to be refractory must be low in iron, silica and alumina, and yet may not be pure. The deposits which are sufficiently pure to use in furnaces where the highest demands are made come from Styria and other parts of Austria-Hungary. The deposits are most carefully mined, the mineral sorted from impurities, ground, mixed sometimes with a suitable bond such as tar or in some cases with little refractory plastic clay, dried and burned several times at a high temperature. These are the most useful bricks for the modern practice of metallurgy.

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In lead-silver smelting practice they make the most economical lining in softening and cupelling furnaces. In the metallurgy of antimony they are used in both shaft and reverberatory furnaces; in tin and arsenic furnaces magnesia is equally satisfactory, and it makes an economical lining in copper and steel practice. The linings of the bath of open hearth copper and steel furnaces are now almost invariably made of magnesia brick. To the copper metallurgist this means the saving of time, money and the physical energy expended on the weekly clayings of the lining, which are costly, and retard work in plants using the fire brick lining. Since the large modern furnaces and fore hearths are placed out of commission on account of their lining being eaten rather than on account of the fore hearth "freezing up," it has been found profitable in the long run to line these with magnesia. We are just entering on the area of basic copper converting when the linings of our copper converters are of magnesia instead of silica clay. These magnesia-lined converters already in use give great satisfaction, and smelt a charge of 2000 pounds per converter. Magnesia is the most satisfactory material to use in electric furnace work and makes a particularly good crucible.

Of the neutral refractories chromite is of the greatest importance to the iron, copper, antimony and tin metallurgists. It is used as a buffer lining between the bath lining of magnesite and the wall lining of fire clay, preventing any reaction between the basic and acid bricks. In the French antimony works it is used as lining in the reduction hearth furnaces; and in the metallurgy of tin it is, and should be still more, used for the bottom and sides of the hearth. In open hearth iron and copper furnaces which use a magnesite bottom, chromite is laid in between the hearth and the foundation of fire brick. Chromite of satisfactory quality is found in Greece and New Caledonia; some is found in California. It should be fairly low in iron and with only sufficient clay content to enable it to bond.

The use of steatite (magnesia and alumina silicate) is a comparatively modern innovation, for use principally in electric furnaces. Perhaps the most recent, or at any rate, the most satisfactory of the more recent introduced refractories is carbo-

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rundum firesand or that silicide of carbon which is produced in an amorphous condition just outside the region of heat at which crystalline carborundum is produced by the combination of silicon with carbon at the intense heat of the electric arc furnace. Carborundum enjoys wide-spread use both as a protective paint for preserving bricks against acid fume and slag and also in form of bricks made by mixing the fine carborundum with a small quantity of fire clay or lime.

Bauxite has not come into more general use on account of its quality of shrinkage. Chemically it is very inert, it may be bonded easily into a brick of unusual strength, but in all practice known the material has shrunk sufficiently to imperil the structure in which it was used.

A. J. Aubrey (Electrochemical and Metallurgical Industry, Vol. IV, page 52) claims that bauxite bricks and blocks made by the Laclede Fire Brick Co., of St. Louis, successfully stood some severe tests and he would argue the superiority of bauxite to magnesia in certain operations in the metallurgy of iron and of lead and to fireclay brick in certain industrial furnaces such as rotary cement kilns. The chief sources of the ore are in Arkansas, New Mexico, Georgia and Alabama. The crude bauxite is washed to remove some of the free silica, calcined, at cone 12, when the water of combination amounting to 30 per cent. of the raw ore is expelled. The bauxite shrinks considerably, particularly between temperatures of cone 9 and cone 12. The washed, calcined, Arkansas bauxite analyses:

Mechanical water	0.88%
Silica	6.40%
Iron sesquioxide	1.43%
Alumina	87.30%
Titanium oxide	3.99%

The calcined material may be bonded with fire clay, sodium silicate or lime and made into brick or tiles, which, after burning at a high temperature in downdraft kilns, are said to be sufficiently strong to stand a crushing strength of 10,000 pounds per square inch. The calcination may be done in a rotary kiln. A brick 9″ × 4½″ × 2½″ weighs 7.5 pounds. In a test made by the St. Louis Portland Cement Co., a lining 6″ thick in a 6′ rotary

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kiln, 60′ long, which burned pulverized coal, was removed after a continuous run of eleven months. During the time 75,000 barrels of cement had passed over the lining and the average loss of the blocks was about 2½″. It is possible that the future may develop uses in the chemical industry for this material.

Of the other neutral refractories I would refer to the growth of the plumbago crucible industry; to the wider uses given to carborundum and similar artificial compounds; to the efforts being made to realize the value of steatite; and to the Norton Company's refractories such as "Alundum."

DISCUSSION.

Prof. Parmelee: I would like to ask Mr. Havard about the temperature, whether he meant centigrade?

Prof. Havard: Yes sir, 1,600 degrees.

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A COMPARISON OF TEN WHITE ENAMELS FOR SHEET STEEL.

By ROBERT D. LANDRUM.

This paper is the record of the manufacturing and description of the physical properties of ten white enamels. It is given not with the idea of presenting to ceramic literature a set of commercial formulas, but to illustrate a method for testing, arranging the data, and arriving at the comparative values of any enamels upon which it might be desirable to experiment.

The ten enamels are those given in the "Taschenbuch für Keramiker, 1911,"[1] pages eighteen and nineteen. It should be stated, however, that some changes have been made in the milling where it was deemed necessary, and also that a feldspar high in silica has been used where the formula calls for pure feldspar.

All the materials, except the borax and the saltpeter, were finely ground. Crystals of these were used. The enamel batches were weighed, a kilogram at a time, on a balance sensitive to one hundredth of a gram. They were then very thoroughly mixed and were smelted, 200 grams at a time, in a gas-fired crucible furnace,[2] at temperatures varying from 1050° to 1200° C. This smelting required from twelve to twenty-five minutes and, as is the custom in practice, the molten enamel was poured into cold water to facilitate subsequent grinding.

The resulting frits were milled—after drying—with the required amount of tin oxide, clay, magnesia and water, about four hundred grams at a time, in a small porcelain ball mill. (This mill is manufactured by the Abbé Engineering Co., N. Y., and is illustrated on page eleven of their catalogue.) The time required for milling varied from $3\frac{1}{2}$ to $6\frac{3}{4}$ hours.

The wet enamel from the mill was slushed upon miniature wash basins which had been previously coated with a good cobalt groundcoat. After drying and burning, a second coating of the same white enamel was applied. Both white cover-coats were applied as thin as possible and were burned in the regular muffle furnaces.

These dishes were then tested as to their resistance against

[1] Published by the Keramische Rundschau, Berlin, N. W., 21, Germany.

[2] See E. H. Sargent's Catalogue No. 2098 for illustration and description of this furnace.

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corrosion by acetic acid; their behavior during rapid expansion and contraction; and their brittleness, elasticity and adhesiveness under punishment by impact; and were examined as to their opacity, gloss, etc., as a finished ware.

METHODS FOR TESTING THE WARES.

TEST AS TO CORROSION BY ACETIC ACID.

Each dish was carefully dried and weighed correctly to 0.0001 gram; and 15 cc. of 20 per cent. acetic acid[3] (20 per cent. by volume of 99.5 per cent. acid) were measured into it. It was then placed on a gas-fired hot plate and boiled to dryness, the plate being so regulated that about thirty minutes were required to bring the vessel to dryness. The enameled dish was then washed out thoroughly with distilled water, rinsed, dried on the hot plate, cooled in a desiccator and again weighed. The difference in weight is the amount of enamel dissolved by the acid, and is recorded as "Acid Loss." The ten enamels were then arranged in a list according to their relative resistance to corrosion, the dish losing the least being first, and so on. The position of each enamel in this list is also given under "Acid Loss."

TESTS OF ADHESION UNDER RAPID EXPANSION AND CONTRACTION.

Test 1.—Twenty-five cubic centimeters of water were heated to boiling in the dish, on a wire gauze over a Bunsen flame, and the dish was then plunged into cold water. The effect of this treatment on the enamel was recorded.

Test 2.—The dish from Test 1 was dried, heated on the wire gauze over the Bunsen flame for one minute, and then plunged into cold water and any results noted.

Test 2½.—In the dish from Test 2 a few cubic centimeters of water were boiled away—over the Bunsen flame as in the other two tests—and then the dish was allowed to remain, dry, over the flame for one minute and was again plunged into cold water. (This test may seem a duplication of the one above. It is not; many commercial wares fail with this test as it is especially severe.)

Test 3.—The dried dish from Test 2½ was very gradually heated in the blast flame until the bottom became red-hot. The results of this rapid expansion were noted.

[3] This has been shown to be about the strongest mixture of acetic acid and water, as measured by its action on an enamel. See Trans. A. C. S., Vol. XIII, pp. 494–501.

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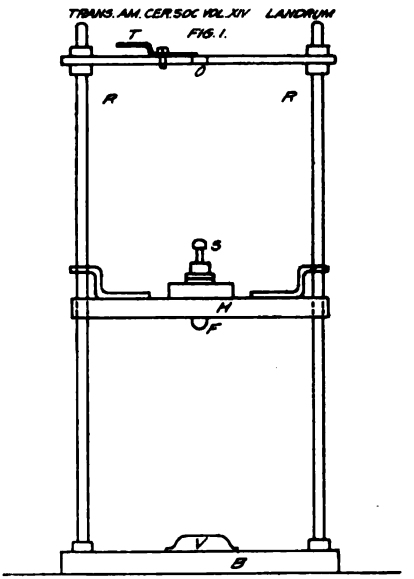
Test 4.—While the dish was still red-hot from Test 3 it was plunged into cold water and the effect of this rapid contraction upon the enamel coating was recorded.

A description of the behavior of each enamel under these tests is given under "Expansion and Contraction," and it is to be noted that when a test is not mentioned the ware was unaffected by it. Again the enamels have been listed, this time according to their adhesiveness under rapid changes of temperature, and their position in this list is also given under "Expansion and Contraction."

TEST AS TO ADHESION UNDER PUNISHMENT BY IMPACT.

A testing machine, by means of which a five-pound hammer



Impact testing machine.

with a three-quarter inch rounded head can be dropped twenty and one-quarter inches onto the middle of the bottom of the inverted basin, was used. The sample dishes were weighed correctly to 0.01 gram before and after the hammer was dropped upon them, and the grams loss and a brief description of the effect upon the enamel coating is recorded under "Loss under Hammer."

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As before, the enamels have been arranged in a list which shows their relative adhesion under punishment by impact.

EXAMINATION AS TO OPACITY.

The finished dishes were arranged in a series according to their opacity, and their position in this series as well as other details as to their appearance are given under "Appearance of the Ware."

ARRANGEMENT OF THE DATA.

It is the custom of the Lisk Manufacturing Company's laboratory to make a complete record of each enamel on a single sheet of special form, and although this cannot be followed exactly in publishing this article, the general arrangement and form of report will be retained.

Immediately under the heading of the enamel the batch mix in percentages and the calculated graphic formula is given, and under the latter the oxygen ratio and the ratio of the silica

Material.	Formula	Equivalent weight	Loss on ignition	Cost per pound
Feldspar[4]	0.45 Na_2O, 0.39 K_2O, 0.06 CaO, Al_2O_3, 7.11 SiO_2	602	1.43%	$0.0035
Borax	Na_2O, $2B_2O_3$, $10H_2O$	382	47.0	0.0375
Quartz	SiO_2	60	.....	0.0025
Cryolite	$2Na_3AlF_6$	420	20.0	0.0600
Soda	Na_2O, CO_2	106	41.5	0.0085
Fluorspar	CaF_2	78	28.2	0.0045
Calcite	CaO, CO_2	100	43.9	0.0060
Saltpeter	K_2O, N_2O_5	202	53.4	0.0525
Carb. magnesia	MgO, CO_2	84	52.1	0.0800
Magnesia	MgO	40	.....	0.1000
Clay	Al_2O_3, 2.8 SiO_2, 1.6 H_2O	300	10.0	0.0100
Tin oxide	SnO_2	151	.....	0.4600

[4] Chemical analysis of feldspar:

	Per cent.
Silica	70.66
Alumina	16.85
Potash (K_2O)	5.93
Soda (Na_2O, by diff.)	4.61
Lime (CaO)	0.52
Carbon dioxide	0.41
Water	1.02
	100.00

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to the boric anhydride (SiO_2/B_2O_3). The oxygen ratio is given considering Al_2O_3 both as a base (ORb) and as an acid (ORa). Following these ratios is the calculated loss on smelting.

A chemical analysis of each of the materials used was made, and from them the following formulas were derived. These and the other constants given in the table above were used in making the calculations.

A brief description of the action of each enamel during smelting and of the resulting frit is given. The milling follows in percentages *of the weight of frit charged*. Thus "12 per cent. tin oxide" means "12 grams of tin oxide to each hundred grams of frit." Water is added to each milling equal to 50 per cent. of the weight of the frit.

The latter part of the record of each enamel needs no further explanation.

The Charts.—Figs. 2 and 3 show a method of arranging all the data in regard to an enamel in such a form that it may very easily be compared with any other enamel. The data of the enamels may be separated by cutting along the horizontal lines of the chart and these slips can be arranged in any order desired for making comparisons. This is especially desirable in a series where but one factor is changed at a time.

The Photographs of the Dishes.—The two half-tones show the effect of the "Hammer Test" and the "Expansion and Contraction Tests" upon both the outside and inside enamel coatings of the ten wares.

Remarks.—The types of these enamels are so different that the writer will not try to draw any conclusions. In figuring the graphic formulas the customary method has been used. In figuring the oxygen ratio, the tin oxide and the fluorine have been ignored. This is incorrect in almost every case, for it has been proved by experiment that only about 20 per cent. of the fluorine is driven off, and it is also a fact that some of the tin oxide combines to form stannous silicate. This is especially shown in Enamel X, for although this melted enamel contains 11.7 per cent. of tin oxide, it is a transparent glaze. Enamel II also illustrates this, for although its oxygen ratio is 4.5 when figured in the ordinary way, it is one of the most easily smelted of the enamels under discussion.

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TRANS. AM. CER. SOC VOL. XIV — FIG. 2 — LANDRUM

ENAMEL	GRAPHIC FORMULA	ORb	ORa	SiO_2/B_2O_3	MILLING	LOSS IN SMELTING	COST PER HUNDRED POUNDS	OPACITY	ACID LOSS	ADHESION UNDER RAPID EXP+CONT	ADHESION UNDER IMPACT	ADHESION AVERAGE	FINAL RATING
I	.497 Na_2O, .186 K_2O, .278 CaO, .039 MgO } .299 Al_2O_3 { 2.513 SiO_2, .262 B_2O_3, .599 F_2	3.1	6.7	9.6	12% SnO_2, 7% Clay	17.34%	$6.70	4TH	5TH 1.01 mg	2	5TH 1.07 gram	3RD	2ND
		38.6%	15.4%	19.0%	11.7%	×	1.3%	6.5%	6.5%	1.0%	×		
II	.563 Na_2O, .131 K_2O, .306 MgO } .090 Al_2O_3 { 1.636 SiO_2, .396 B_2O_3, .525 SnO_2	4.5	—	4.1	2.1% SnO_2, 4.3% SiO_2, 8% Clay	19.89%	$15.07	2ND	1ST 0.0 mg	1ST	3RD 1.02 gram	1ST	1ST
		×	22.9%	29.7%	×	11.7%	×	×	8.0%	×	3.7%	24.0%	
III	.894 Na_2O, .097 K_2O, .009 CaO } .147 Al_2O_3 { 2.217 SiO_2, .632 B_2O_3, .399 SnO_2	4.4	6.8	3.5	10% Clay	21.08%	$9.81	7TH	2ND 0.16 mg	3RD	9TH 1.31 gram	4TH	4TH
		22.0%	30.0%	17.5%	×	13.5%	×	×	2.0%	×	×	15.0%	
IV	.834 Na_2O, .098 K_2O, .007 CaO, .061 MgO } .249 Al_2O_3 { 2.571 SiO_2, .272 B_2O_3, .721 F_2	3.4	6.8	9.5	6.67% SnO_2, 4.44% Clay	16.61%	$5.03	5TH	3RD 3.3 mg	10TH	6TH 1.07 gram	9TH	5TH
		23.5%	16.2%	31.4%	15.7%	9.3%	×	×	3.1%	×	0.8%	×	
V	.504 Na_2O, .176 K_2O, .320 CaO } .281 Al_2O_3 { 2.447 SiO_2, .284 B_2O_3, .636 F_2	3.1	6.6	8.6	11.76% SnO_2, 5.88% Clay	17.86%	$6.67	3RD	4TH 8.4 mg	6TH	2ND 1.0 gram	5TH	3RD
		35.3%	16.8%	20.5%	12.0%	×	2.0%	7.0%	6.4%	×	×	×	

All enamels smelted at 1050° to 1200° Centigrade for from 12 to 25 minutes. All millings include ¼% MgO

FELDSPAR — BORAX — QUARTZ — CRYOLITE — SODA — FLUORSPAR — CALCITE — SALTPETER — $MgCO_3$ — MAGNESIA — TIN OXIDE

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TRANS. AM. CER. SOC. VOL. XIV — FIG. 3. — LANDRUM

ENAMEL	GRAPHIC FORMULA	ORb	ORa	SiO_2/B_2O_3	MILLING	LOSS IN SMELTING	COST PER HUNDRED POUNDS	OPACITY	ACID LOSS	ADHESION UNDER RAPID CONT-EXP.	ADHESION UNDER IMPACT	ADHESION AVERAGE	FINAL RATING
VI	.648 Na_2O .109 K_2O .243 CaO } .198 Al_2O_3 { 1.558 SiO_2 .458 B_2O_3 .452 F_2 .2225 SnO_2	2.7	5.0	3.8	93% SnO_2 7% Clay	20.71%	$11.10	1ST	8TH 19.0 mg	7TH	8TH 1.13 gram	7TH	6TH
	32.0%	26.0%	8.0%	5.0%	9.0%	6.0%	×	3.0%	×	×	11.0%		
VII	.500 Na_2O .179 K_2O .282 CaO .039 MgO } .303 Al_2O_3 { 2.525 SiO_2 .255 B_2O_3 .598 F_2	3.0	6.7	9.9	11.1% Clay	17.09%	$2.17	9TH	9TH 20.4 mg	9TH	4TH 1.06 gram	8TH	9TH
	39.0%	15.0%	19.0%	12.0%	×	1.0%	7.0%	6.0%	1.0%	×	×		
VIII	.661 Na_2O .111 K_2O .228 CaO } .208 Al_2O_3 { 1.508 SiO_2 .463 B_2O_3 .215 F_2 .293 SnO_2	2.7	5.0	3.3	7.87% SnO_2 4.5% Clay	20.87	$12.08	6TH	10TH 35.3 mg	4TH	1ST 0.56 gram	2ND	8TH
	36.4%	27.8%	1.3%	×	11.3%	6.3%	×	2.0%	×	×	13.9%		
IX	.670 Na_2O .062 K_2O .005 CaO .263 MgO } .228 Al_2O_3 { 2.406 SiO_2 .323 B_2O_3 .834 F_2	3.4	6.5	7.4	10% Clay	15.48	$2.87	8TH	7TH 15.9 mg	8TH	10TH 1.42 gram	10TH	10TH
	17.7%	20.5%	35.3%	13.4%	1.0%	×	×	1.0%	×	31.5%	×		
X	.841 Na_2O .142 K_2O .017 CaO } .283 Al_2O_3 { 2.033 SiO_2 .625 B_2O_3 .227 SnO_2	3.2	6.8	3.2	6.4% Clay	21.33	$7.01	10TH	6TH 11.9 mg	5TH	7TH 1.09 gram	6TH	7TH
	45.7%	32.0%	×	×	11.4%	×	×	1.7%	×	×	9.2%		

Hammer weighing 5 lbs and falling 20½ inches used in Impact Test
20% Acetic acid used in Acid Test.

FELDSPAR — BORAX — QUARTZ — CRYOLITE — SODA — FLUOR SPAR — CALCITE — SALTPETER — $MgCO_3$ — MAGNESIA — TIN OXIDE

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ENAMEL I.

Feldspar	38.6%	0.497 Na_2O	0.299 Al_2O_3	2.513 SiO_2
Quartz	19.0	0.186 K_2O		0.262 B_2O_3
Borax	15.4	0.278 CaO		0.599 F_2
Cryolite	11.7	0.039 MgO		
Saltpeter	6.5			
Calcite	6.5	ORb = 3.1 ORa = 6.7 SiO_2/B_2O_3 = 9.6		
Fluorspar	1.3			
Mg carbonate	1.0			

Loss on Smelting.—17.34 per cent.

Milling.—Four hours with 12 per cent. tin oxide, 7 per cent. Vallendar clay and $^1/_4$ per cent. magnesia.

Smelting.—Smelted at about 1200° C., hundred gram batches required about 15 minutes. The melted enamel is quite viscous and is inclined to be lumpy.

The Frit.—The frit is fairly opaque but is translucent in spots.

Acid Loss.—0.0101 gram (fifth in list).

Expansion and Contraction.—This ware was unaffected by heating to redness in blast flame (Test 3) and came off only over a medium sized surface on the outside and a comparatively small surface on the inside when plunged, red-hot, into cold water. This enamel is very adhesive, according to this test, and is second only to Enamel II.

Loss under Hammer.—This was 1.07 grams, and the manner in which the enamel comes off shows it to be of average brittleness and elasticity. It is placed fifth in the list according to this test, but it is to be noticed that all the enamels, excepting VIII, which is much the best, and IX and III, which are much the worst, stand very close together.

Appearance of the Ware.—This ware sets a very high standard in its appearance and is much more opaque than many with higher tin oxide content. In fact, it would be marketable with a much smaller proportion of this oxide added at the mill, and with this change would be a good commercial enamel. As it stands, it is fourth in the list, according to opacity.

Cost.—The cost of the materials for the finished enamel is $6.70 per hundred pounds; and this could be reduced by using

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less potassium nitrate, and, as said before, by using less tin at the mill.

Remarks.—If the cost is not considered, but considering everything else, this is the second best enamel of the ten. If cost is considered, it is the *very best.*

ENAMEL II.

Quartz	29.7%	0.563 Na_2O	1.636 SiO_2
Tin oxide	24.0	0.131 K_2O	0.396 B_2O_3
Borax	22.9	0.306 MgO	0.525 SnO_2
Sodium carbonate	11.7		
Saltpeter	8.0	OR = 4.5	SiO_2/B_2O_3 = 4.1
Magnesia	3.7		

Loss on Smelting.—19.89 per cent.

Milling.—Six and three-fourths hours with 4.3 per cent. quartz, 2.1 per cent. tin oxide and 8 per cent. Vallendar clay.[5]

Smelting.—Smelted at about 1200° C., hundred gram batches required about 15 minutes. To get the maximum opacity it was necessary to mechanically stir just before pouring. The viscosity was medium and melt was free from lumps.

The Frit.—The frit was extremely opaque and quite hard and tough.

Acid Test.—The acid test showed this enamel to be absolutely unaffected by 20 per cent. acetic acid solutions, and thus it is first in the list as to resistance to corrosion by acid.

Expansion and Contraction.—When plunged, red-hot, into cold water (Test 4) this enamel came off over very small surfaces, both inside and outside, and in such a manner that it is easily singled out as the most adherent enamel of the ten. Few enamels have even been tested by the writer that have withstood sudden changes of temperature as well as this one.

Loss under Hammer.—This was 1.02 grams. This enamel is of average brittleness and elasticity and is placed third in the list as to adhesion under punishment by impact, but an examination of the sample used for this test shows that it is not as well suited to the ground coat as is Enamel I.

Appearance of Ware.—This ware is very opaque, and it cer-

[5] Necessary for correct slushing but not given in original directions.

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tainly should be, as the finished enamel contains something like 32 per cent. of tin oxide. It is second in opacity only to Enamel VI, which contains a little over 23 per cent. of tin oxide when on the ware. This enamel is so opaque that it may be put on in very thin coatings. This is an advantage, as the thinner the enamel is applied the more durable the product.

Cost.—The cost of this enamel is $15.07 per hundred pounds, and this would make it entirely impractical to use on a commercial ware. It is a freak enamel in every sense, and is of interest on this account.

ENAMEL III.

Borax	30.0%	0.894 Na_2O	0.147 Al_2O_3	2.217 SiO_2
Feldspar	22.0	0.097 K_2O		0.632 B_2O_3
Quartz	17.5	0.009 CaO		0.399 SnO_2
Tin oxide	15.0			
Sodium carbonate	13.5	ORb = 4.4	ORa = 6.8	SiO_2/B_2O_3 = 3.5
Saltpeter	2.0			

Loss on Smelting.—21.08 per cent.

Smelting.—Smelted at about 1200° C. for 15 minutes or less; the melt pours with medium viscosity.

The Frit.—The frit was creamy-white and very opaque. Some of the tin oxide remained in suspension, but, except for this, the frit was homogeneous.

Milling.[6]—Five hours with 10 per cent. Vallendar clay, and $^1/_4$ per cent. magnesium oxide.

Acid Loss.—The acid loss was but 0.0016 gram. This is remarkably low and places this enamel second in the list as to acid resistance.

Expansion and Contraction.—This too is an excellent enamel, according to the manner in which it withstands punishemnt by rapid changes of temperature. It was unaffected by any of the tests up to Test 4 and when plunged, red-hot, into water during this test came off in flakes, both from the inside and outside of the dish. Very little steel was laid bare, but the surface of the ground coat enamel which was exposed is larger than on either Enamel I or Enamel II. This enamel is placed third on the list.

Loss under Hammer.—This was 1.31 grams. This shows

[6] Original directions gave no milling.

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up the chief fault in this enamel—brittleness and lack of elasticity—and places it next to last in the list, arranged in accordance with their relative ability to withstand punishment by impact.

Appearance of Ware.—Considering the fact that this enamel contains about 19 per cent. of tin oxide when on the ware, it is very poor in opacity indeed. The writer has made many white enamels with no other opacifier than cryolite that were more opaque than this one. It is fourth from the poorest among these ten.

Cost.—The cost of this enamel is $9.81 per hundred pounds. If the cost is not considered, this enamel stands fourth, considering all its properties.

ENAMEL IV.

Quartz	31.40%	0.834 Na_2O	0.249 Al_2O_3	2.571 SiO_2
Feldspar	23.50	0.098 K_2O		0.272 B_2O_3
Cryolite	15.70	0.007 CaO		0.721 F_2
Borax	16.20	0.061 MgO		
Sodium carbonate	9.30			
Saltpeter	3.10	ORb = 3.4	ORa = 6.8	SiO_2/B_2O_3 9.5
Magnesia	0.80			

Loss on Smelting.—16.61 per cent.

Smelting.—Smelted at about 1100° C., four hundred gram batches required 15 minutes. The viscosity of the melt was medium.

The Frit.—The frit had little, if any, opacity and with a smelting of 18 minutes became a clear glass.

Milling.—Four hours with 6.67 per cent. tin oxide, 4.44 per cent. Vallendar clay, and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0033 gram, placing this enamel third on the list.

Expansion and Contraction.—While being heated to dryness (Test 2½) innumerable "nail chips" flew off, both from the inside and outside surface, and when heated to redness in the blast flame (Test 3) a few more came off. When plunged red hot into cold water (Test 4) the coatings peeled off over medium sized surfaces, leaving the ground coat almost bare. Notwithstanding the apparent adhesiveness under Tests 3 and 4, the utter failure of this enamel under Test 2½ causes it to be deemed

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the poorest of the ten, according to its resistance to punishment by rapid changes of temperature.

Loss under Hammer.—This was 1.07 grams; and although this is not far different from several others, the manner in which the remaining enamel adhered places this ware sixth in the list.

Appearance of the Ware.—Although this enamel contains but eight per cent. of tin oxide in its finished coating, it is opaque enough to be placed fifth in the list. The gloss is quite poor.

Cost.—The cost of this enamel is $5.03 per hundred pounds. Its final rating places it fifth in the list.

ENAMEL V.

Feldspar	35.30%			
Quartz	20.50	0.504 Na_2O	0.281 Al_2O_3	2.447 SiO_2
Borax	16.80	0.176 K_2O		0.284 B_2O_3
Cryolite	12.00	0.320 CaO		0.636 F_2
Calcite	7.00			
Saltpeter	6.40	ORb = 3.1	ORa = 6.6	SiO_2/B_2O_3 = 8.6
Fluorspar	2.00			

Loss on Smelting.—17.86 per cent.

Smelting.—Smelted at about 1100° C., in from 18 to 20 minutes. The melt, when poured, was very thick and sticky. This mixture is inclined to melt unevenly and should be mechanically stirred for best results.

The Frit.—The frit has a translucent white color, fairly good for the amount of cryolite it contains. It is not noticeably hard and tough.

Milling.—Five hours with 11.76 per cent. of tin oxide, 5.88 per cent. of Vallendar clay, and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0084 gram. This is of about the same acid resistance as the best wares on the market and is excelled only by Enamels I, II and IV in this list.

Expansion and Contraction.—When boiled to dryness on asbestos gauze, this enamel chipped slightly (Test 2½) but was not further affected when plunged into cold water. When heated to redness (Test 3) more chips flew off the outside and the inside enamel blistered somewhat. When plunged, red hot, into cold water according to Test 6, the enamel came off very badly from both surfaces of the dish, and much steel was laid bare. This

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enamel stands sixth according to this test, and is typical of the action of many of the wares on the market.

Loss under Hammer.—This was 1.00 gram, showing this enamel to be quite elastic. It stands next to the best, according to this test.

Appearance of the Ware.—This ware is quite opaque, standing third among the ten, but when one considers that 12 per cent. of cryolite was used in the smelt and that the finished enamel contains 12 per cent. of tin oxide, he comes to the conclusion that much of the color must have been lost.

Cost.—The cost of this enamel is $6.67 per hundred pounds and its final rating places it third best, when all its physical properties are considered.

ENAMEL VI.

Feldspar	32.00%	0.648 Na_2O	0.198 Al_2O_3	1.558 SiO_2
Borax	26.00	0.109 K_2O		0.415 B_2O_3
Tin oxide	11.00	0.243 CaO		0.452 F_2
Sodium carbonate	9.00			0.222 SnO_2
Quartz	8.00			
Fluorspar	6.00	ORb = 2.7	ORa = 5.0	SiO_2/B_2O_3 = 3.8
Cryolite	5.00			
Saltpeter	3.00			

Loss on Smelting.—20.71 per cent.

Smelting.—Smelted at about 1150° C. in from 20 to 22 minutes. The viscosity of this enamel was rather low.

The Frit.—The frit was creamy-white and quite opaque but inclined to be non-homogeneous. Threads of this enamel were brittle.

Milling.—Five hours with 9.3 per cent. tin oxide, 7 per cent. Vallendar clay, and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0190 gram, placing this enamel eighth on that list.

Expansion and Contraction.—During Test 3 a few large chips came off while the dish was being heated to redness in the blast flame. When plunged red-hot into cold water, a large surface of the ground coat was laid bare on the outside, but the inside was affected very much less. This enamel is seventh best, according to this test.

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Appearance of the Ware.—This is the best appearing enamel of the ten, and its great opacity is not to be wondered at when we consider that as a finished enamel it contains about 23 per cent. of tin oxide. The gloss is splendid.

Loss under Hammer.—This is 1.13 grams, which is the average, but places this enamel third from the last when listed according to its relative resistance to punishment by impact.

Cost.—The cost of this enamel is $11.10 per hundred pounds; but as much more oxide of tin has been used than is necessary for even a very high grade ware, this could be greatly reduced. Considering everything, this is the sixth best enamel of the ten.

ENAMEL VII.

Feldspar	39.00%	0.500 Na_2O	0.303 Al_2O_3	2.525 SiO_2
Quartz	19.00	0.179 K_2O		0.255 B_2O_3
Borax	15.00	0.282 CaO		0.598 F_2
Cryolite	12.00	0.039 MgO		
Calcite	7.00			
Saltpeter	6.00			
Fluorspar	1.00	ORb = 3.0	ORa = 6.7	SiO_2/B_2O_3 9.9
Mg carbonate	1.00			

Loss on Smelting.—17.09 per cent.

Smelting.—Smelted at about 1200° C. The melt poured thin and somewhat lumpy.

The Frit.—The frit was quite translucent and non-homogeneous, a hard glassy frit.

Milling.—Three and one-half hours with 11.1 per cent. Vallendar clay and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0204 gram, or next to the worst in the ten.

Expansion and Contraction.—This enamel chipped somewhat when boiled to dryness in Test 2½, but no more chipping was observed while heating to redness in blast flame (Test 3). When plunged, red-hot, into cold water (Test 4) the enamel adhered fairly well, especially on the inside, but the failure in Test 2½ places this enamel next to the poorest, according to this test.

Loss under Hammer.—This was 1.06 grams and this ware comes fourth as to its adhesiveness under punishment by impact.

Appearance of Ware.—Considering the fact that there is no oxide of tin in this enamel, it is quite opaque indeed and deserves

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further trial with tin oxide added at the mill. Even as it stands, it is more opaque than Enamel X, which contains almost 12 per cent. of tin oxide. It stands next to the last in the list, arranged according to the relative opacity of the ware.

Cost.—On account of the absence of tin oxide in the make-up of this enamel, its cost is but $2.17 per hundred pounds. With the proper addition of this oxide at the mill, this enamel would cost about $5.00 per hundred pounds. Everything except the cost considered, this enamel is rated as ninth best.

ENAMEL VIII.

Feldspar	38.40	0.661 Na_2O	0.203 Al_2O_3	1.509 SiO_2
Borax	27.80	0.111 K_2O		0.463 B_2O_3
Tin oxide	13.90	0.228 CaO		0.215 F_2
Sodium carbonate	11.30			0.293 SnO_2
Fluorspar	5.30			
Saltpeter	2.00			
Quartz	1.30			

ORb = 2.7 ORa = 5.0 SiO_2/B_2O_3 = 3.3

Loss on Smelting.—20.87 per cent.

Smelting.—Smelted at about 1200° C. for from 15 to 18 minutes. The viscosity was rather low. Although the melting point of this enamel is low, it was difficult to drive off all the CO_2.

The Frit.—The frit was creamy and very opaque, but rather brittle.

Milling.—Four hours with 7.87 per cent. tin oxide, 4.5 per cent. Vallendar clay, and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0353 gram. This is entirely too high for a cooking utensil and places this ware last in the list as to its resistance to corrosion by acetic acid.

Expansion and Contraction.—While heating this dish to redness, a few chips flew off and when plunged, red-hot, into cold water (Test 4) the enamel flaked off over quite a large surface, but only to the ground coat and even this was fairly well covered by the adhering cover coat. This ware stands fourth according to this test.

Loss under Hammer.—This was 0.56 gram, so that according to this test the enamel is very excellent indeed. It stands punishment by impact better than any of the rest.

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Appearance of Ware.—The opacity of this ware is very low, considering the fact that it contains 25½ per cent. of tin oxide. It stands sixth when listed according to opacity.

Cost.—The cost of this ware is $21.08 per hundred pounds. This is the most expensive of the wares, except one, and yet it stands sixth according to opacity and eighth when everything is considered.

ENAMEL IX.

Quartz	35.30%	0.670 Na_2O	0.228 Al_2O_3	2.406 SiO_2
Borax	20.50	0.062 K_2O		0.323 B_2O_3
Cryolite	19.40	0.005 CaO		0.834 F_2
Feldspar	17.70	0.263 MgO		
Magnesia	3.50			
Sodium carbonate	1.80	ORb = 3.4	ORa = 6.5	SiO_2/B_2O_3 = 7.4
Saltpeter	1.80			

Loss on Smelting.—15.48 per cent.

Smelting.—Smelted at about 1200° C. for from 15 to 18 minutes. This enamel was difficult to pour from the crucible. The enamel was quite viscous and lumpy.

The Frit.—The frit was very hard and, although quite opaque, was translucent in spots.

Milling.[7]—Three and a half hours with 10 per cent. Vallendar clay and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0159 gram, or seventh in the list of ten enamels.

Expansion and Contraction.—When plunged, red-hot, into cold water (Test 4) this enamel came off over a large surface on the outside and a small surface on the inside of the dish. The steel was laid bare in many places. In the list of wares, arranged according to their resistance to punishment by change of temperature, this enamel stands eighth, as it scaled slightly during Test 2½ when water was boiled to dryness in it.

Loss under Hammer.—This was 1.42 grams, which is more than any of the other dishes lost, and places this enamel last in the list.

Appearance of Ware.—This enamel is remarkable in its opacity, all of which comes from the cryolite and clay. It con-

[7] Milling not given in original directions.

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tains no tin oxide and stands eighth in the list according to opacity.

Cost.—The cost is but $2.87 per hundred pounds. With sufficient oxide added at the mill to bring this up to a remarkable standard, this enamel would cost about $5.50 per hundred pounds. Considering everything, this is the poorest enamel of the ten.

ENAMEL X.

Feldspar.....	45.70%	0.841 Na_2O		2.013 SiO_2
Borax.....	32.00	0.142 K_2O	0.283 Al_2O_3	0.625 B_2O_3
Sodium carbonate..	11.40	0.017 CaO		0.227 SnO_2
Tin oxide.....	9.20			
Saltpeter.....	1.70			

ORb = 3.2 ORa = 6.8 SiO_2/B_2O_3 = 3.2

Loss on Smelting.—21.33 per cent.

Smelting.—Smelted at about 1050° C. for 20 minutes; this enamel became transparent, although it contains 9.2 per cent. tin oxide. Its viscosity was medium.

The Frit.—The frit was a colorless glass, comparatively hard and quite tough.

Milling.—Four and one-fourth hours with 6.4 per cent. Vallendar clay and $^1/_4$ per cent. magnesia.

Acid Loss.—0.0119 gram, placing this enamel sixth in the list.

Expansion and Contraction.—While heating to redness in the blast flame, the enamel bubbled slightly, and when plunged, red-hot, into cold water, came off to the steel over a small surface on the inside and a larger surface on the outside. This enamel stands fifth, according to this test.

Loss under Hammer.—This was 1.09 grams, which places this cover coat seventh in the list.

Appearance of Ware.—Although this enamel contains 11.7 per cent. tin oxide, it stands last in opacity, being nothing more nor less than a clear glass.

Cost.—The cost of this enamel is $7.01 per hundred pounds.

DISCUSSION.

Mr. Rankin: Mr. Landrum, I would like to ask if you have ever made any experiments in the line of substituting sodium nitrate for potassium nitrate?

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Mr. Landrum: I have made experiments on a small scale and a large scale. The substitution of sodium nitrate for potassium nitrate is successful only where you can make routine analyses of the sodium nitrate. Sodium nitrate takes up water from the air, and thus varies in strength. In the sheet steel enameling industry, the variation of water content will spoil the enamel unless this is taken into account.

I worked in one place where they determine this very nicely by weighing about ten or fifteen pounds and then drying and reweighing it, thus getting results which were as accurate as taking a smaller sample and testing it in the laboratory.

Mr. Staley: I wish to say that I consider this a very able paper.

The Germans do not use the empirical formula in their enamel industries to any large extent. They publish their results in percentage of the various oxides. When it comes to fluorides, they publish their results in percentage of the various fluorides. I think that is a fairly good way. In my own papers, I prefer to consider the melted weights of the various minerals; consider the feldspar, for instance, as feldspar rather than as split up into the oxides. The method I use is very similar to that of the Germans. Mr. Landrum advocates the use of empirical formulas in connection with batch weights. This divergence in methods of calculation shows very nicely that, provided a man works in a systematic manner and has enough experience, he can get results from a variety of methods of calculation.

Enamels III and X are two cases where there are high sodium and potassium oxides and practically no other basic oxide. I believe that early in the history of this Society Mr. Burt gave the results of some experiments in which he showed that you can melt tin oxide and sodium carbonate, or tin oxide and potassium carbonate, together and get a clear glass. It is known that there are sodium stannates and potassium stannates in existence which are translucent. I think it is more plausible to say that in a material as basic as enamel the loss in opacity is due to the fact that the potash and soda are high rather than to attribute the poor opacity to any hypothetical effect that the alkaline earths have in preventing the tin from forming stannous

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silicate. I have always found that, with a given amount of tin oxide, when sodium and potassium run up the opacity decreases. To verify Mr. Landrum, I find that increasing calcium or barium oxide increases the opacity. To my mind this means simply that opacity was increased by decreasing the percentage of sodium and potassium.

Mr. Purdy: I would like to ask Mr. Landrum if it makes any difference in the power of tin oxide to produce opacity, whether you frit it or use it raw?

Mr. Landrum: Yes, there is a very marked difference. This has already been brought out in the Transactions. It never pays to put tin oxide in the smelt for opacity.

I have found, however, that it is good practice to put a small amount of tin oxide in the smelt for gloss. In this case you get no opacity from the tin oxide. For maximum color, the tin oxide should be added at the mill.

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DETERMINING THE COST OF ENAMELED STEEL COOKING UTENSILS.

By J. B. SHAW, Ellerslie, Md., and LUCIAN SHAW, West Lafayette, Ohio.

The manufacture of steel cooking utensils embraces a great number of different items of great variety of size and shape and, consequently, differing in the cost of manufacture. In order to avoid selling some articles at a profit and others at a loss, it is necessary to know as exactly as possible the cost of each individual item.

From the nature of the business, it is readily seen that it is impossible to determine exactly the cost of any single item; but it can be found to a very close approximation, and he who would tread on safe ground should not be satisfied until he has determined as nearly as possible the exact cost of every item he manufactures.

The following is an outline of the method used in figuring a cost system for The West Lafayette Mfg. Co.

This paper does not contain all of the data obtained because the method used for determining the cost of one item will apply to any other item, with perhaps a few exceptions; hence, one typical item was taken and all data obtained thereon are given.

The labor at this plant is very largely piece work and where it is not piece work the cost was gotten by timing the operator without his knowledge while working on 100 pieces of ware.

The item taken to illustrate the work is the 14 qt. hollow-handle dish pan. For convenience the following outline is used:

- Machine room cost.....
  - Labor
    - Cutting blanks
    - Oiling blanks
    - Pressing shapes
    - Spinning
    - Beading
    - Riveting
  - Steel
    - Sheet steel
    - Rivets
    - Handles

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- Enamel room cost
  - Labor
    - General
    - Scaling
    - Pickling
    - Dipping
    - Beading
    - Burning
  - Material
    - Acid
    - First coat enamel
    - Second coat enamel
    - Finish enamel
    - Fuel
- Packing room cost
  - Labor
    - Packing
    - Sorting
    - Wrapping
  - Material
    - Straw and paper
    - Crates
- Other expenses
  - Office
  - Management
  - Power
  - Interest
  - Depreciation
  - Sundry

MACHINE ROOM.

Labor:

Cutting blanks—piece work	0.06 per hundred
Oiling blanks	0.03 per hundred
Pressing shapes	0.07 per hundred
Spinning	0.10 per hundred
Beading	0.07 per hundred
Riveting	0.60 per hundred
Total labor	0.83

Steel.—The blank used for the 14 qt. dish pan is a circle 22 inches in diameter, 25 gauge steel, cut from a square 22 × 22 inches, bought in this shape.

100 sheets 22 in. × 22 in. × 25 G. weighs	285 lbs.
100 circles 22 in. diameter 25 G. weighs	219 lbs.
Scrap	66 lbs.
Scrap in beading 100 pans	2 lbs.
Total scrap to sell	68 lbs.

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285 lbs. steel at 2.09½ per 100 lbs.	$5.97
68 lbs. scrap at 0.40 per 100 lbs.	0.27
Total cost of steel for 100 pans.	$5.70
Cost of rivets	0.02
Cost of 200 handles	1.40
Total cost steel	$7.12

ENAMEL ROOM.

Labor:

Sealing	$0.12 per hundred
Pickling	0.17 per hundred
Dipping first coat	0.25 per hundred
Dipping second coat	0.25 per hundred
Dipping finish coat	0.41 per hundred
Beading	0.10 per hundred
Burning ground coat	0.50 per hundred
Burning second coat	0.55 per hundred
Burning finish coat	0.60 per hundred
General labor	1.20 per hundred
Total labor	$4.15 per hundred

Materials.—Acid: The acid used for pickling is commercial hydrochloric acid, costing about 1 cent per lb. Fifteen lbs. acid used for 100 pans at 1 cent per lb. is 15 cents per hundred.

First Coat Enamel: The cost of the enamel per hundred lbs. is figured as follows:

Raw material 500 lbs. costs	$9.00
Labor required for fritting	0.25
Fuel in fritting 500 lbs., 11 bu. coal at 6 cents	0.66
Frit resulting 400 lbs.	$9.91
$9.91 ÷ 400 = $2.48 per 100 lbs. of frit.	

First coat enamel:

100 lbs. frit	$2.48
10 lbs. raw material	0.10
110 lbs. unground	$2.58
Burned weight is 108.5 lbs. cost	$2.58
Cost on ware of 1 lb	0.0238

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White enamel frit:

Raw material 500 lbs	$12.50
Labor mixing and fritting	0.25
Fuel fritting 11 bu. coal at 6 cents	0.66
Frit resulting 410 lbs	13.31

$13.31 ÷ 4.10 = $3.25 per 100 lbs.

Enamel:

Frit	3.25
Raw material 20 lbs	5.50
120 lbs	$ 8.75
Burned weight 118.5 lbs	8.75
1 lb. costs	0.0738

Finish Coat.—This finish coat at present is white inside and mottled blue and white outside, the mottled effect being produced by simply throwing colored enamel from a brush on the ware just after dipping in white.

The colored enamel is produced from white residue by grinding with colored stain. The residue is the drippings from the ware in finishing plus the washings from all ware which is spoiled before burning the white. The amount of white enamel which finally reaches the residue tub is a variable factor and can only be roughly estimated.

The stain used in making the colored enamel costs about $1.00 per lb. and about $1^1/_2$ per cent. is added to the residue, hence, the finish color costs about $1.50 per 100 more than the white.

The ratio of color to white used in finishing the ware is about as 15 to 100.

In reading the last three paragraphs one is strongly impressed with the amount of guess work contained therein, but because of admixtures of color and white in greatly varying proportion there is no method by which accurate determinations can be made. Personal observation and experience have convinced the writers that these estimates are not far wrong.

Then—100 lbs. white at	$7.38	$7.38
15 lbs. color at	0.0888	1.33
115 lbs. finish		8.71
100 lbs. finish enamel		7.57

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Enamel for Black Beading.—This is the finish put on the bead and handles of the ware, generally black. It is made from first coat residue and raw materials by fritting them together. The bead is a very small item and as its cost differs so slightly from that of white frit, it has not been determined separately, but weighed in with the second coat enamel.

In determining the amount of each enamel used, 100 pans were weighed just before dipping in first coat, second coat, and finish, and after being finished.

Raw wt.	1st coat wt.	2nd coat wt.	Finished wt.
234 lbs.	248 lbs.	286 lbs.	326 lbs.
Deduct	234 lbs.	248 lbs.	286 lbs.
Total enamel	14 lbs.	38 lbs.	40 lbs.

14 lbs. first coat at	0.0238	0.33 per 100 pans
38 lbs. second coat at	0.0738	2.80 per 100 pans
40 lbs. finish coat at	0.0757	3.03 per 100 pans
Total cost of enamel		$6.16 per 100 pans
Fuel for muffle, 12 bu. at 6 cents		$ .72 per 100 pans

This fuel factor runs constantly 3 bu. per hour, regardless of what is being burned.

PACKING ROOM.

Labor:	
Labor packing	$0.50 per hundred
Sorting and wrapping	0.40 per hundred
Materials:	
Straw and paper	0.20 per hundred
Crates	2.00 per hundred
Total packing room cost	$3.10 per hundred

GENERAL EXPENSE.

The remaining items are figured from the normal capacity of the plant, six hundred 14 qt. dish pans per 24 hours.

In figuring the cost of enamels, the power for grinding was not included in the cost. The power given here includes all power required for running machine room and grinding enamels, lighting, heating and drying.

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Power—Gas	$2.00	
Labor	2.00	
	4.00 ÷ 6 =	$0.67 per 100 pans
Management		2.00 per 100 pans
Office expense		0.33 per 100 pans
Interest		1.75 per 100 pans
Sundry, including grates, repairs, depreciation, etc.		1.00 per 100 pans
		$5.75 per 100 pans

SUMMARY OF COST.

Total cost of steel per 100 14 qt. dish pans		$7.12
Total machine room labor		0.83
Total enamel room labor		4.15
Total enamel room material.		
Acid	0.15	
Enamel	6.16	
Fuel	0.72	7.03
Total packing room cost		3.10
Other expenses not included above		5.75
Total cost		$27.98

The above figures represent very closely the cost of 14 qt. dish pans at this plant, at this time. It must be admitted that these figures will vary somewhat with different workmen and different enamels; and whenever conditions are materially changed, this process should be repeated in order to keep the cost figures up to date.

Knowing the cost of manufacture and the percentage of "Number Ones" and "Seconds" in the finished ware, it is simple enough to figure which side of the ledger will contain the balance at the end of the year.

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THE CAUSE AND CONTROL OF CRAZING IN ENAMELS ON CAST IRON.[1]

By HOMER F. STALEY.

INTRODUCTION.

Crazing and its converse shivering in enamels on cast iron are such complicated phenomena that it is advisable to give a preliminary statement of how I purpose to treat the subject. It must, first, be understood that in this discussion I am dealing with enamels applied by the American process, that is, a thick coat of opaque glass sifted dry onto a thoroughly fused and extremely thin ground coat. I do not intend to discuss the problems as they appear in enamels applied by the wet process nor when a relatively thin coat is applied to a thick and only partially fused opaque ground coat. The latter process is employed in some European factories but is no longer in use, to the writer's knowledge, in this country. I shall first give the practical methods of controlling general crazing in enamels on cast iron and next a discussion of the causes of general crazing and shivering. Then, I shall take up cases of crazing and shivering that occur only in particular patterns or shapes. Since in these cases the connection between the cause and control of the crazing is so very close, the cause and method of control will be treated at the same time.

In the treatment of all practical points in the control of crazing, I shall be as plain and explicit as possible. It is desired that these parts of the paper may be available, not only to trained chemists, but also to those practical men in the enameling business who have not had the advantage of a technical education. The section of the paper dealing with the cause of general crazing will necessarily be more abstract in its thought.

PART I.—GENERAL CRAZING.

A. THE CONTROL OF GENERAL CRAZING.

Occurrence of General Crazing.—It sometimes occurs that there is a decided tendency for a large proportion of the ware

[1] Contribution from the Ceramic Engineering Laboratory of the Ohio State University.

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being made in a plant to craze or to shiver. This general crazing or shivering is usually much more easily remedied than the trouble arising in single patterns or shapes to be discussed later. Nevertheless, it is certainly desirable that the treatment of such cases be fully set forth together with as much of an explanation for the same as we can reach.

Seger's Rules.—Any discussion of crazing must go back to the work of Seger and his well-known rules for correcting the defects of fritted glazes by altering their composition as follows:

I. On the Occurrence of Crazing.—(A) By an increase of the silica content and decrease of the fluxes raising the alumina at the same time, if this is necessary to prevent devitrification. With an increase of the silica and also the alumina content, an elevation of the melting point of the glaze takes place.

(B) By an increase of the boric acid at the expense of the silica, leaving the other ingredients of the glaze unaltered. By this, a lowering of the melting point of the glaze is accomplished.

(C) By substitution of one of the fluxes with a high equivalent weight (and, therefore, giving a glaze with a low percentage of silica) by one having a lower equivalent weight (and, therefore, giving a glaze with a higher percentage of silica). An elevation of the melting point of the glaze is coincident with this change.

II. On the Occurrence of Shivering, Cracking of the Edges, etc.—Reverse the above rules.[2]

Segers's Rules A and C in Simple Language.—The wording of the rules will be mystifying to most enamel workers. They are not accustomed to talking about "equivalent weights." This language is due to the custom, established by Seger, of recasting the composition of glazes into certain units for purposes of calculation and comparison. The ideas back of this system were the expectations that the use of these units would enable the ceramist to see the chemical similarities or dissimilarities in glazes, and that chemically similar glazes would have like physical properties. Neither of these expectations have been realized to any great extent.

So enthusiastic have ceramists been about this method of

[2] The Collected Writings of H. A. Seger, page 581, published by the American Ceramic Society, Columbus, Ohio.

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calculation, and so fixed have they become in the habit of doing their thinking in this tedious and involved method that most of them have failed to see the other aspect of the rules as presented by Seger.

Rules A and C can be combined and made to read, practically in the words of Seger, as follows: *On the occurrence of crazing, increase the percentage of silica, or silica and alumina, thus rendering the glaze more infusible.* This rule is well known to all enamel workers, and, in fact, to the majority of enameling plant workmen, who never heard of Seger or chemical equivalents. It is common parlance around an enameling room to say: "*If the enamel crazes, harden it; if it shivers, soften it.*"[3]

As we have intimated, the use of chemical equivalents, empirical formula, oxygen ratio, and all the other "impedimenta" of ceramic calculations have never come into general use among enamel workers. Nor does it seem to me that it is desirable that they should. Even in comparatively simple glaze mixtures, this method of calculation has not given the results that were expected from it. This is on account of the fact that the physical condition of the ingredients and their state of chemical combination is fully as important as the final chemical composition of the entire batch. In the much more complicated mixtures that we have in iron enamels, the use of "empirical formulae" is very laborious and serves to give little or no insight into the factors controlling the physical properties of the fused enamel. It is much more simple for an enamel maker to go about curing a case of general crazing or shivering by his plain "harden or soften" rule than it would be for him to attempt the same thing by the use of empirical formulae and Seger's rules A and C. Whichever way he works, he will do the same thing when he comes to weigh his batch—in cases of crazing, lower the percentage in the melted enamel of those ingredients that render the enamel fusible; in the case of shivering, raise the percentage of these.

Application of the Simple Rule.—As we have stated, the simple statement of Seger's rules A and C found in the "harden

[3] "Harden" is used by enamelers in the sense of "render more infusible." "Soften" is used in the sense of "render more fusible."

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or soften" rule of the enameling shop is usually applied in cases of general crazing, or shivering. In many cases, it is effective. The actual variation in the enamel batch differs widely among enamel workers. Red lead is most often used as a variant. Variation in the amount of fluorspar of cryolite is sometimes used. We know of one enamel maker who for several years successfully controlled crazing and shivering of this kind by varying soda ash. In our own experience, we have varied red lead, fluorspar, cryolite, barium carbonate, soda ash, borax, glass-makers sand, flint, and feldspar.

Probably the safest ingredient to vary is feldspar. Since this is present in such large amount in the batch, a moderate variation does not make a radical change in the general make-up of the enamel. Thus, there is little danger of running into difficulties, such as loss of luster, tendency to blister, change in tint, loss of opacity, etc.

We, therefore, submit the following rule:

Rule I. When general crazing occurs in a fusible enamel, increase the feldspar. When general shivering occurs in a refractory enamel, decrease the feldspar.

Seger's Rule C.—This rule states that crazing may be reduced by increase of the boric acid at the expense of the silica, and that a lowering of the fusing point of the glaze accompanies this change. In the terms of the enamel makers, this means that crazing may be reduced by substituting boric acid for flint in the proportion of 124 parts of raw boric acid for 60 parts of flint. The validity of this rule as a cure for crazing in glazes has been called in question by Purdy and Fox[4] and others. The effectiveness of this rule for application in curing all cases of general crazing has been questioned by the author of this paper.[5] If a soft enamel crazes, substitution of boric acid for flint will not cure the crazing. However, we sometimes find general crazing in hard enamels in which any attempt to cure the crazing by application of Seger's rules A and C, either in their complex form as used by some clayworkers or in their simplified form as

[4] Trans. Am. Cer. Soc., Vol. IX, p. 177.
[5] Ibid., Vol. X, p. 120.

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used by enamel makers, results only in making the crazing worse. This treatment may go so far as to render the enamel so hard as to be unworkable, without decreasing the crazing. We believe and have actually demonstrated that in many cases this is due to the enamel being too hard for the ground coat. It is well known that an immature glaze or enamel is more liable to craze than a fully matured one. Even if the hard enamel is properly matured, crazing may take place. This latter phase of the subject will be treated in the next section.

When crazing occurs in a refractory enamel, increase in any of the ingredients that render the enamel more fusible makes the enamel less liable to craze. For instance, increase of red lead or zinc oxide and decrease of feldspar have been found effective at different times. We have found that a modified form of Seger's rule C, consisting of increase of boric acid without decreasing silica, is the safest plan to follow. Boric acid may be increased by simply putting in the hydrous boric acid. In case it is desired to increase boric acid by putting in borax, a reduction may be made in the soda ash in order that the sodium in the enamel may not be raised. The addition of 38 lbs. of borax and removal of 10.5 lbs. of soda ash will have the same effect as the addition of 25 lbs. of raw boric acid. This gives us all the advantage of a decrease in coefficient of expansion, if the crazing should happen to be due, in part, to high coefficient of expansion in the enamel, and, at the same time, gives a more fusible enamel better suited to the ground coat.

We, therefore, submit the following:

Rule II. When general crazing occurs in a refractory enamel, increase boric acid.

Relation of the Fusibility of the Ground Coat to That of the Enamel.—As we said above, general crazing sometimes seems to be due to a lack of conformity between the fusibility of the ground coat and that of the enamel, which lacked of conformity results in poor attachment between the enamel and the iron. We have known cases where an enamel that was giving good results crazed or shivered when applied over a ground coat that had given good results with another enamel. In fact, in extreme cases, both crazing and shivering would occur even on the same

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piece of ware. In these cases the trouble was remedied by changing the fusibility of either the enamel or the ground coat.

This lack of conformity may, of course, take two forms: First, the enamel may be too refractory for the ground coat. In this case, if the enamel is properly fused, the ground coat is simply burned to a cinder under the enamel and the bond between the enamel and iron destroyed. If the ware is fired only until the ground coat is at its best strength, the enamel coat is not only rough but immature and, consequently, liable to craze. Second, the enamel may be too fusible for the ground coat. In this case the enamel matures before the ground coat has become fluid enough to take a proper hold on the iron, and, consequently, no firm bond between the enamel and iron is ever formed. The obvious remedy is to bring the maturing point of the enamel and the temperature range at which the ground coat is at its best closer together. Since at most plants either the enamel or ground coat will have a fusibility suited to the general working conditions of the enameling room, the remedy will consist in an alteration of the fusibility of the other coat. Incidentally, we might say that in some cases it would probably be advisable to secure a ground coat with a longer temperature range.[6]

We, therefore, submit the following:

Rule III. In all cases of general crazing or shivering and especially in cases where these defects occur together, see to it that the fusibility of the ground coat and enamel properly conform.

Advantages of a Thin and Uniform Coat of Enamel.—It has been my own experience, working in several shops and with many different enamels, that the thinner and more uniform the enamel coat, the less liable it was either to craze or shiver. As far as I have been able to ascertain, this has been the experience of all enamel makers.

We, therefore, submit the following:

Rule IV. Have the enamel applied to the ware in as thin and as uniform a coat as possible.

Variations in Strength and Elasticity of Enamels.—Various

[6] Some valuable suggestions in this regard will be found in a paper by Mr. John H. Coe, entitled "A Comparison of Commercial Ground Coat Enamels for Cast Iron." Trans. A. C. S., Vol. XIII, p. 531.

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enamels of the same fusibility show minor differences in their tendency to craze and to shiver. In some cases, increase in the percentage of a certain fluxing material at the expense of another fluxing material, in such proportions as to keep the fusibility of the enamel the same, always tends to reduce crazing. I have found this to be true of boric oxide. In other cases, increase in the percentage of a certain ingredient, keeping the fusibility the same, tends to accentuate the defect in fit to which the given enamel is subject. If the enamel tends to craze, the change makes the crazing worse; if it tends to shiver, the substitution increases the shivering. I believe, as the result of my experience, that the fluorides have this tendency. In still other cases, the substitution of a certain ingredient for others, keeping the fusibility the same, minimizes the fault of fit to which the enamel is subject. The use of zinc oxide has, according to my observations, this effect when substituted for other fluxing materials. Zinc oxide, however, must be used with caution, for it forms compounds that are easily crystallized. When this occurs, the enamel loses not only in strength but also loses its luster. It has always seemed to me that those enamels in which feldspar alone was used as a hardening material were not as liable either to craze or shiver as those in which flint or sand was used to a considerable extent. The high flint enamels always appeared to be more brittle. It is extremely difficult to get absolute assurance on these points, and I simply state them as my personal experience and would be pleased to have the opinion of other enamel makers on these questions.

B. THE CAUSE OF GENERAL CRAZING.

Object in Discussing Theories of Crazing.—The writer is free to confess that he has little interest in theoretical considerations as to the cause of crazing. To know how to control crazing seems to him to be of much more importance than to prove or disprove a theory of the cause of the phenomenon. Our only object in discussing the theory of the cause of crazing can be that we may thus arrive at more efficient methods of controlling it.

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THE DIFFERENCE IN COEFFICIENT OF CONTRACTION THEORY OF CRAZING.

The Theory.—The theory of crazing that has found most adherents is the difference in coefficient of contraction theory. The adherents of this theory hold that crazing is due to a difference in thermal coefficient of contraction and expansion of the glaze and body. As applied to enameled iron, the theory is as follows: Crazing and shivering are due to a difference in coefficient of contraction and expansion with temperature of the enamel and iron. On cooling a piece of ware, a strain is set up between the enamel and iron, due simply to this difference in rate of contraction with change of temperature. If the enamel has the higher coefficient of contraction, there is a tendency for crazing to result. If the enamel has the lower coefficient, there is a tendency for the enamel to be pushed off the ware, resulting in shivering, or chipping, at the edges and on sharply convex curves. If there is no difference in the rate of contraction, there is no strain set up and consequently no tendency to craze or shiver.

Seger's Belief in this Theory.—Seger believed fully in the difference in coefficient of contraction theory of crazing and shivering. Therefore, since he found the above rules would stop crazing and shivering in the class of glazes with which he worked, he naturally thought these rules were rules for varying the coefficient of contraction of the glaze. It is to be noted that, although Seger did more than any other man to establish this theory of crazing in the minds of ceramists, he never did any experimental work to prove the validity of the theory. That rules A and C work in glazes and in enamels in the majority of cases of general crazing or shivering there can be no question. Rule C has been found to work in glazes only under certain conditions, and the same holds true in enamels as has been shown. That these rules are a direct means of varying the coefficient of contraction is far from being established.

Limitations of this Theory.—In discussing this theory of the cause of crazing, we must recognize one very important limitation of its application that is not always taken into account by its adherents. Strains set up due to a difference in coefficient of the enamel and iron would be only such strains as would arise

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if we should start with no strain in the enamel or iron and with every particle of the enamel and iron at exactly the same temperature and should then cool or heat in such a manner that every particle of enamel and iron would undergo exactly the same change in temperature at exactly the same rate. Under these conditions, if it were properly supported and free from the iron, the sheet of enamel could be cooled or heated as rapidly as desired without any strain being set up. The same would be true of the iron casting. Therefore, it is evident that this theory does not cover the crazing and shivering caused by the strains that arise for a variety of reasons in a rapidly cooled piece of glass of large size and varying thickness. Such strains would render a piece of glass of the size and shape of the sheet of enamel as worthless as a lot of Prince Rupert's drops if the glass vessel should be cooled under the same conditions that a piece of enameled iron actually is. This would be true even if the sheet of glass were properly supported and free from strains due to its own weight, which is not true in an enameled iron casting.

These various causes of strain will be taken up later. It is well, however, to keep the possibility of their existence in mind while we are discussing the strains supposed to be caused by a difference in coefficient of contraction.

Comparison of this Theory with Actual Occurrence of Crazing and Shivering.—Let us see how this theory fits in with the observations as to the circumstances under which crazing and shivering occur in enamels.

First. The strains due to a difference in coefficient of contraction between the enamel and iron should consist of either a simple tension or thrust effecting every part of the piece in equal degree and every piece made of the same enamel and same iron. In the usual enameling plant, this would mean that there would be a decided tendency for a large proportion of the ware being made to develop either crazing or shivering. We have found that such a condition sometimes exists.

Second. We have found that, the rest of the composition being kept the same, the fusibility and tendency to craze may

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be decreased by increasing SiO_2 and *vice versa*, the infusibility and tendency to shiver may be decreased by decreasing SiO_2. It is well known that increase of SiO_2 decreases the coefficient of any workable glass or enamel. This point fits in with the theory.

Third. When crazing occurs in a refractory enamel, it may be reduced by making changes that also make the enamel more fusible. If we render it more fusible by adding a substance such as lead oxide, we are raising the coefficient of contraction (as we will see shortly). This in respect to variation of coefficient of contraction is contrary to the theory. However, if we consider that this change simply permits a better condition in the ground coat, it is not in contradiction to the theory. For, as we will see under our next point, it would be perfectly possible that an enamel having proper attachment to the iron could better withstand a large tension due to a slightly larger difference in coefficient of contraction, than another enamel, having poor attachment, could withstand the smaller strain due to a small difference in coefficient. If we make the enamel more fusible by increasing boric acid, which would lower the coefficient, we have no appearance of contradiction to the theory.

Fourth. We found that both tendency to craze and to shiver are decreased by proper attachment of the enamel to the iron. In view of my remarks that according to this theory there would be no strain due to difference in coefficient if there were no attachment, it would seem that the fact that proper attachment gives less defects than poor attachment would be contrary to the theory. On reflection, however, we see that if there is any attachment at all, there would be a strain set up. Each part of the enamel between two points of attachment has to bear the strain due to the over-contraction or expansion of the strip of enamel between these two points of attachment. The greater the distance between two points of attachment, the greater the strain each part of the strip has to bear and the greater the danger of rupture in the weakest part.

We would expect that, if this be true, in some instances the point of attachment would break instead of the enamel, thus

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giving a larger strip free from points of attachment to the iron with each part of the strip bearing a correspondingly heavier strain. This could go on indefinitely until finally, if the enamel had the greater coefficient, we would get a large fracture with the enamel on either side of the fracture not attached to the iron. We actually find such large and distinct fractures. In enameling shop vernacular, they are known as "lifts" because the enamel seems to have been raised or lifted free from the iron. On the other hand, we would expect to find, when the enamel had the smaller coefficient, large areas shivering off the iron. We sometimes actually find this condition. We can conclude, then, that the observed relation between proper attachment of the enamel to the iron is not a contradiction to the difference in coefficient of contraction theory of crazing, but that it shows the existence of one very important modifying circumstance.

Fifth. We observed that the thinner the coat of enamel, the less the tendency both to craze and to shiver. That a thin enamel should be less liable to craze than a thicker one is in direct contradiction to the coefficient of contraction theory. If crazing is simply a matter of failure to withstand a straight pull, a thick enamel shou'd be less liable to craze than a thin one. The observed facts lead us to think that elasticity or ductility must be a factor in the power to withstand tendency to craze. The relation between elasticity and thin section in any substance is well known. That the thicker coat is more liable to shiver is no evidence for or against the theory. It simply shows that, whatever the cause of the strain, the thicker coat is more able to break the bond between the enamel and iron.

Summary of Relation of Fact to Theory.—In summing up the relation of the actual circumstances, under which crazing and shivering occur, to the difference in coefficient of contraction theory we find:

First. Several of the observed circumstances fit in well with this theory. This, of course, does not necessarily prove the theory. An equal number might be made to fit in with some other theory. In such a complicated problem as the cause of

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crazing, several circumstances can be made to fit in with any theory, no matter how fantastic.[7]

Second. Several circumstances under which general crazing occurs seem to be in contradiction to the difference in coefficient theory.

Third. Several circumstances under which general crazing occurs seem to indicate that factors other than relative coefficient of expansion must be taken into account.

ACTUAL MEASUREMENT OF COEFFICIENT OF EXPANSION OF ENAMELS.

Works of Winkelman and Schott.—Winkelman and Schott determined the actual coefficient of expansion with temperature of thirty different glasses. They have published[8] the following coefficients, by which the percentages of the constituent oxides of a glass are to be multiplied in order to obtain by addition ten million times the value of the cubical expansion per degree centigrade of the glass.

Na_2O	10.0	BaO	3.0
K_2O	8.5	ZnO	1.8
CaO	5.0	SiO_2	0.8
Al_2O_3	5.0	B_2O_3	0.1
PbO	3.0	MgO	0.1

Work of Mayer and Havas.—Mayer and Havas have done a vast amount of valuable work in measuring the coefficients of expansion of enamels.[9] These experimenters confirm the figures of Winkelman and Schott within 2 per cent., except that for PbO

[7] An instance is found in Hopkins' "oxygen strain" theory of crazing. Hopkins has found that by making certain variations in a glaze he can increase or decrease the tendency to craze. By a rather complicated system of calculation, he has figured that in making these variations in a systematic manner he has also systematically varied the ratio of the molecular volume of the oxygen in the glaze formula to the molecular volume of the metallic elements in the glaze formula. This he does, assuming that the various elements when in combination in the glaze have the same molecular volume as when free. Hopkins points out the relation between these calculated molecular volume ratios (he calls them oxygen strains) and crazing. For the variations that he presents in his papers, Hopkins is absolutely right. This relation does hold. Therefore, Mr. Hopkins says that crazing is due to "oxygen strain" and presents his calculations to prove his point. Now the point to the whole thing is that in controlling the tendency to craze and shiver Hopkins has made exactly the same variation in the batch of his glazes that ceramists have made for years. The latter said they were controlling the coefficient of contraction; Hopkins says he was controlling the "oxygen strain." One has as many points to support his theory as the other.

[8] Ann. d. Phys. v. Chem., LI, 735, and "Jena Glass" by Hovestadt, page 217.

[9] Sprechsaal, XLII, 497; XLIV, 1885, 207, 220.

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which they make 4.2. In addition they have found values for enamels containing opacifiers as follows:

Na_3AlF_6	7.4	TiO_2	4.1
NaF	7.4	Fe_2O_3	4.0
ThO_2	6.3	NiO	4.0
Cr_2O_3	5.1	Sb_2O_5	3.6
BeO	4.7	CaF_2	2.5
CoO	4.4	MnO_2	2.2
AlF_3	4.4	CuO	2.2
CeO_2	4.2	ZnO	2.1
PbO	4.2	SnO_2	2.0

They found the coefficient of expansion of enamels for sheet steel to average around 0.0000300 and that of the steel used in making enameled sheet steel wares to average around 0.0000400. They, therefore, believe that the enamel on enameled sheet steel utensils is under considerable compression. This opinion is verified by the well known fact that the enamel on this sort of ware seldom crazes but is rather prone to shiver. Mayer and Havas believe that, owing to the limitations set on variation in composition of this type of enamel by practical consideration of manufacture and necessary properties in the furnished ware, it is not possible to produce an enamel for sheet steel with a coefficient much more than 75 per cent. as high as that of the steel. They conclude that success in making this type of ware must depend on care in manufacture and especially on producing ware with a thin coat of enamel and one of uniform thickness in order that the elasticity of the enamel may be developed to the highest degree.

Using the values of Mayer and Havas, I have calculated 10,000,000 times the value of the cubical expansion of the twelve enamels, the recipes for which I published in Volume XIII, page 519, Transactions of the American Ceramic Society. They are as follows:

I	310	VII	298
II	317	VIII	290
III	317	IX	296
IV	327	X	292
V	319	XI	292
VI	319	XII	311

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The cubical coefficient of expansion of cast iron, when multiplied by 10,000,000, has been found to be close to 310. It will be seen that the coefficient of the enamels varies around that of cast iron. This may explain how an enamel on cast iron may develop either crazing or shivering, while sheet steel enamels do not craze.

Using these different enamels on the same cast iron, I have not noticed any particular tendency for the enamels with high coefficients to craze or for those with low coefficients to shiver.

Work of Purdy and Potts.—It is of interest to note in this connection that Purdy and Potts[10] measured the coefficient of expansion of a large number of porcelain bodies. These bodies were then all glazed with the same glaze. These investigators found that the crazing which appeared bore no direct relation to the coefficient of contraction of the porcelain body.

THE RELATION OF ELASTICITY AND STRENGTH OF THE ENAMEL TO CRAZING.

This whole discussion of the control and cause of general crazing brings us around to the realization that there must be factors operating other than simply a difference in coefficient between the enamel and the iron. Upon consideration, we see that whether a given material will be fractured by a strain depends upon at least three factors.

First. The amount of strain. In the case of strain due to a difference in coefficient of expansion, the amount of strain would be proportional to the difference in coefficient.

Second. The ability of the substance to yield to the strain, *i. e.*, its elasticity or ductility.

Third. The ability of the substance to withstand the strain, in other words, its strength.

It is readily seen that, since all three of these factors must be operative in all cases, the tendency for general crazing or shivering to occur will not be in all cases proportional to the difference in coefficient of expansion.

A large difference in coefficient might be offset by high strength or elasticity (ductility) in the enamel. For instance,

[10] Trans. A. C. S., Volume XIII, page 431.

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our experience has led us to believe that in an enamel of given fusibility a high content of zinc oxide has a favorable influence in counteracting crazing. By reference to the work of Winkelman and Schott, we find that a content of zinc oxide exerts a decidedly favorable influence both on the strength[11] and elasticity[12] of glass. We have discussed the close connection between high elasticity and a thin and uniform coat of enamel. Again, we spoke of the action of B_2O_3 in tending to reduce crazing in an enamel of given fusibility. Winkelman and Schott found that a content of B_2O_3 had a decided effect in reducing the coefficient of contraction[13] of glasses and also a favorable effect in increasing their elasticity. The strength of the enamel is, as we have seen, dependent to a large extent upon proper attachment to the iron. Since these three factors always act concomitantly and we have no means of determining which one is of paramount importance, we believe that we are not justified in ascribing crazing to one of them alone. We would have as much reason for ascribing crazing to poor strength or elasticity in an enamel as to ascribe it to high coefficient of contraction. In either of these cases, we would be wrong, for we would be taking into consideration only one out of three coördinate factors. Moreover, to the mind of the writer, it seems that it must be a rare case indeed in which crazing or shivering occurs, due to the play of these three factors alone. If the ordinary sheet steel enamel resists the strain due to a difference of coefficient of 25 per cent., the thicker cast iron enamels certainly are able to withstand a possible difference in coefficient of 10 per cent.

UNEQUAL COOLING AND OTHER FACTORS.

While the three factors of difference in coefficient, strength, and elasticity must be always operative in a case of general crazing, they are not by any means the only factors that may be taking part in the production of the phenomenon. It is practically impossible to have every particle of a piece of enameled iron at exactly the same temperature when we start to cool it; and

[11] "Jena Glass," page, 151.
[12] Ibid., page 159.
[13] Ibid., page, 217.

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it is altogether impossible, in the accepted manner of manufacturing, to cool every particle at exactly the same rate. Therefore, in the cooling of any piece of enameled ware, there are set up strains due to lack of uniform cooling. From our knowledge of the effect of such strains on the strength of unannealed glass, we are forced to conclude that these strains must be very severe, much more severe indeed than any strains that might possibly be set up due to a difference in coefficient of expansion between the ordinary enamel and the ordinary cast iron. Two years ago, I expressed my belief that "crazing is caused in the same way that a piece of glass that is not annealed properly is caused to break."[14] I still hold to the opinion that unequal cooling is one of the most potent factors in causing general crazing and shivering in enamels on cast iron.

Likewise, in a case of general crazing or shivering, any or several of the other numerous conditions that produce special crazing may be operating to reinforce the factors that tend to produce general crazing or shivering.

CONCLUSIONS AS TO THE CAUSE OF GENERAL CRAZING AND SHIVERING.

(A) Three coördinate factors must always be operating to effect the fit of an enamel coat on an iron casting: (1) difference in coefficient of contraction and expansion of the iron and enamel; (2) the strength of the enamel, which is largely dependent upon proper attachment to the iron; (3) the elasticity (ductility) of the enamel, which is largely dependent upon a thin and uniform coat. While certain combinations of these factors would tend to produce crazing, and other combinations would tend to produce shivering, it is probably very seldom that a case of shivering or crazing occurs due to the play of these three factors alone.

(B) Unequal cooling is probably the most potent factor in producing general crazing.

(C) Tendency to general crazing or shivering, due to factors mentioned in A and B, may be reinforced by any or several of the circumstances that tend to produce crazing or shivering in special patterns.

[14] Trans. A. C. S., Vol. XII, page 326.

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PART II. SPECIAL CRAZING.

Definition of the Phrase.—Much more common than the occurrence of general crazing is the occurrence of crazing or shivering in ware made over a certain pattern, or on casting made by a certain molder, or in ware that has been enameled by certain workmen. Obviously, such phenomena are not due primarily to the composition of the enamel but to special causes. Such cases of crazing I designate as special crazing or, more properly, crazing due to special causes. In this section I purpose to take up several such cases.

Relation of Special to General Crazing.—It is well to call attention in the very beginning of this discussion to the fact that, just as the causes of special crazing may be auxiliary agents in bringing about general crazing, a tendency toward general crazing or shivering may be an auxiliary cause of special crazing or shivering. The two classes of causes, working together, may cause a rupture that would not appear if only one were operative. Therefore, a rule to be applied in all cases of special crazing or shivering is to minimize as much as possible the tendency to general crazing or shivering. This is to be done, of course, by applying the rules laid down in the first section.

CASE I. THICK SPOTS IN THE CASTING.

EFFECT.

A thick spot in the casting has two effects: First, the thick spot does not heat up as readily as the rest of the casting, and, consequently, the ground coat is not properly fused on it by the time it is at its best strength on the rest of the casting. The result is poor bond between the iron and enamel on the heavy spot. If the piece is fired until the ground coat is properly fused on the heavy spots, there is danger that the ground coat on the rest of the casting will be overfired. The result is a lack of proper attachment between the enamel and iron on the thinner portions of the casting. Second, the thick spots do not cool down as rapidly as the rest of the casting. Therefore, the enamel over the thick spot continues to contract and set after the surrounding enamel is rigid. The result is that this part of the enamel is under special stress and strain.

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The defect due to a heavy spot depends upon the location of the heavy portion and the heat treatment given the casting. The heavy portion may consist of an iron bead on the edge of the casting or of a heavy portion at a convexly curved portion of the casting. If the ground coat is not properly matured on these portions, there will be a tendency for chipping (shivering) to take place, due to the poor bond between the enamel and iron and to the contraction of the enamel on the heavy portion after the surrounding enamel has become rigid. When the casting is heated until the ground coat on the heavy portion is properly matured and the ground coat on the thinner portions of the casting is heated beyond its best strength, the enamel over these thinner portions tend to develop "lifting." A "lift" is, as we have explained, a large distinct crack occurring in an area of enamel that lacks proper attachment to the iron. While by this latter treatment there results proper attachment of the enamel on the thick spots to the iron, the section of the enamel over the heavy spot is still subject to the strains due to the slower rate of cooling of the heavy portion of the casting. The result is that there is some tendency for chipping to occur on the heavy convex curves and beads.

In case the heavy portion is at a concave curve or in a flat surface and the ground coat over it is not properly fused, there is a tendency for fine crazing to occur, due to the location of the area, the poor bond between enamel and iron, and the slower cooling of the heavy portion of the casting. If the bond made by the ground coat is very defective, lifting may result. Sometimes, in portions at the edge of a piece, chipping occurs. In case the piece is heated until the ground coat is properly fused over the heavy portions, there is the liability that the ground coat on the thinner portions will be overheated and that the bond between the enamel and iron at these areas will be thus rendered defective. In this case, the tendency is for the enamel on these areas to develop the defect to which it is subject, crazing or shivering as the case may be. When the bond is very defective, we may have lifting and scaling of the enamel in large flakes. Moreover, crazing is liable to occur at the border of the heavy portion

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owing to the contraction and setting of the enamel in this area after the surrounding enamel has become rigid.

Thus, we see that a heavy spot in the casting may cause either crazing or shivering. It may also cause "lifting" and in extreme cases may be the occasion of the development of crazing and shivering in the same piece.

REMEDIES.

First. Reduce the thickness of the metal as much as possible. At one time, beads were supposed to be a necessary ornament for every lavatory. In late years, beads have been removed from all first-class lines with much improvement in the beauty of the ware and a decided decrease in the amount of defective ware. Thick spots in casting are often due to slipshod methods in pattern making. This is inexcusable, even from the standpoint of economy. The use of a defective pattern in an enameling plant is one of the most extravagant ways of wasting money that can be devised. One of the characteristic differences I have noted in visiting various plants is that the successful plants invariably have good patterns and the unsuccessful ones generally have poor ones. All patterns should be filed to templets, not only on the larger surfaces but also in corners, on rims, etc. Of course, all parts of a pattern can not be of the same thickness, but it is possible to know just how thick each part is.

Especial care should be taken in the design of parts where it is necessary to have a double thickness of metal, as at the overflow channel of a lavatory. I have broken castings and found that, due to carelessness in design of core boxes, there was a thickness of five-eighths of an inch of metal between the overflow channel and the bowl of a lavatory. Is it any wonder that bowls made over that pattern had been giving trouble in the enameling room? Or is it any wonder that firms which habitually use patterns as grossly defective in one way or another as this are not able to compete with more alert concerns? Many of the collars around opening can easily be dispensed with, and others can be made much lighter where they lap over the body of the casting than is the custom in some shops. At a certain plant, considerable trouble was experienced from crazing around the outlet of a certain size roll rim sink. On examination we

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found that the collar of the bell was three-eighths of an inch thick and lapped over the bottom of the sink for one and one-eighth inches. When the pattern was altered so that the collar was only a scant quarter of an inch thick and lapped over only one-half inch, the crazing immediately disappeared. Many other instances of the advantages gained by simple alterations in the thickness of parts of a pattern might be quoted, but space does not permit.

Second. Turn and chill the piece while the ground coat is being fused. This is a trick of manipulation in use at most plants. It consists in removing the piece from the furnace when it has reached a dull red heat, allowing it to cool for a minute or two, then putting it back in the furnace in the reverse position from the one originally occupied. While the heavy spots heat up more slowly than the thinner portions, they also lose the heat they have gained more slowly. The chilling allows the piece to go back into the furnace with the heavy spots considerably ahead in temperature of the thinner spots. Thus, there is a chance that the ground coat on the heavy spots will fuse at the same time that the ground coat on the rest of the casting does. Of course the turning is in the interest of even heating of the casting.

Third. Put a more fusible ground coat on the heavy spot. The object of this is obviously to attempt to have it fuse down at the temperature at which the regular ground coat is at its best strength on the rest of the casting.

Fourth. Provide a ground coat that has a long heat range, *i. e.*, one that fuses at a low temperature and is still good at a high temperature. Such a ground coat will stand large inequalities of temperature in various parts of the casting. The way to go about obtaining such a ground coat is indicated in Mr. Coe's paper, already referred to.

Fifth. Provide an enamel of high elasticity and great strength. We have indicated in a general way in the other section of this paper, how this can be done. The main points to be observed are to have the enamel as high as possible in zinc oxide, high in boric oxide, and to have it applied in a thin and uniform coat.

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CASE II. THIN SPOTS IN THE CASTING.

This is plainly the reverse of Case I and the effect and remedies have been sufficiently indicated under that heading. The only variation in the remedies would be that we would endeavor to make the thin spots thicker instead of thinner and that we would put a more refractory ground coat on the thin spot than on the rest of the casting. Chilling, a good ground coat, and a strong elastic enamel are just as serviceable in the case of thin spots as in that of heavy spots.

CASE III. SHARPLY CONCAVE CURVES AND PROJECTING CORNERS.

EFFECTS.

It is well known, as a matter of experience, that chipping is liable to occur on sharp projecting corners and sharply convex curved portions of a piece of ware. This is probably due, in part, in many cases to the fact that such portions are liable to be especially thick, owing to the difficulty of properly filing the reverse surface in the pattern and of properly molding it in the casting. In addition to this, there is the fact that as the casting cools there is a tendency for the enamel not to follow the decreasing arc of the curve but to split off along lines tangent to it. This tendency to rupture is due to the rigidity or slight elasticity of enamel and comes into play no difference what the relation between the coefficients of contraction of the enamel and iron. If there should be any difference in the coefficients of the enamel and iron, it would act as follows. If the enamel should have the larger coefficient, there would be a tension set up which would tend to cause the enamel to be pulled in two. If the enamel should have the smaller coefficient, it would be thrown into a state of thrust and the tendency would be for the enamel to be pushed off the ware at the sharp curve or corner. Both these latter tendencies would, therefore, simply increase the tendency to rupture, due to lack of elasticity in enamel.

REMEDIES.

First. Avoid sharp corners and make all convex curves with radii as large as possible.

Second. See that the reverse side of convexly curved portions

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of patterns are properly hollowed out. See that such portions are properly molded.

Third. Use an enamel that does not tend to give general crazing or shivering, and one with as much elasticity as possible. The composition of such an enamel has been indicated. It is a soft enamel high in zinc oxide and in boric oxide.

Fourth. Apply the enamel in as thin and uniform a coat as possible. This is in the interest of elasticity in the enamel.

CASE IV. SHARPLY CONCAVE CURVES.

EFFECTS.

Just as there is a tendency for enamel to fly off at a tangent to a convex curve, there is a tendency for enamel to be crushed on a sharply concave curved portion of a casting. As the casting cools, the angle of the concave curve becomes more acute, and the enamel must adjust itself to this sharper angle. This tendency, however, seldom manifests itself in a rupture for the simple reason that the power of enamel to resist such a strain is very great. The power of a glass to resist crushing is very great, as shown by Winkleman and Schott, ten to twenty times as great as its power to resist tension,[15] and in this case the enamel forms a natural brace for itself.

A sharply concave portion of a casting is frequently a cause of defect in the enamel for an entirely different reason. Owing to the method of applying the enamel by sifting it on as a dry powder, it is very difficult to enamel the area around a sharply concave curve without getting an extra heavy coat of enamel in the sharply curved portion or corner. This is especially true if the sharp curve or corner comes at the bottom of a straight area, such, for instance, as at the bottom of the straight back in a "D" shaped lavatory bowl. The defect due to a heavy spot of enamel will be discussed in the next section, but sharply convex curves and corners constitute a special cause for the production of such spots, and so are treated as a distinct case in the list of causes for special crazing.

REMEDIES.

First. Eliminate, as far as possible, sharply concave curves in the casting. At different times, I have had a large number

[15] Ann. d. Phys. und Chem., XLIX, 401. "Jena Glass," by Hovestadt, 151.

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of patterns altered so as to increase the radii of sharply concave curves on the surface. In all these the tendency to crazing in these parts was greatly decreased and in most cases disappeared altogether.

Second. Apply the various rules for avoiding rolls given in the next case.

CASE V. ROLLS.

EFFECTS.

A "roll" is a heavy accumulation of enamel on the surface of a casting. The difference between a roll and a simple thick spot of enamel is that a roll shows some evidence of flow. Practically all excessively thick spots of enamel, such as those that form in corners, become rolls. In addition to this, rolls may be caused by excessive flow in enamel on a straight or a slightly curved surface.

The effect of a roll is to produce a tendency toward crazing, either in the roll or in the enamel close around it. When the ware is cooling, the roll remains hot longer than the thinner coat of enamel surrounding it. The result is that the enamel constituting the roll is contracting after the surrounding enamel has become rigid. Strains are thus set up that cause the crazing and "lifting" mentioned.

REMEDIES.

First. Alter the pattern as directed under Case V so as to reduce the tendency for enamel to lodge in hollows and corners.

Second. Use finely ground enamel. When the enamel is coarse, it does not fuse and adhere readily on being applied to the casting, but part of it drops down and accumulates in piles, especially in corners and hollows.

Third. Use fairly fusible enamel. This is in the interest of having the enamel adhere readily.

Fourth. Have the workmen use mechanically agitated sieves and take especial care in the application and heat treatment of enamel on castings in which rolls tend to form. The surface to which the enamel is being applied should be as nearly horizontal as possible. The enamel should be applied in as uniform a coat as possible. As soon as the enamel ceases to adhere well, applica-

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tion should be stopped. In heating, the ware should not become so hot that there is any large amount of flow in the enamel. These precautions show that in order to minimize the tendency for the formation of rolls, it is necessary to have the enamel applied in a coat so nearly uniform that it is not necessary to have any appreciable flow in the enamel while the ware is in the furnace. Such application is not readily obtained by use of sieves agitated by hand, but is easily obtained by the use of mechanically agitated sieves.

CASE VI. BEADS OF ENAMEL.

EFFECTS.

"Beads" are small rolls around the edge of an enameled surface. They are caused by the pressing up of the enamel into a roll when a workman tries to cut off the part of the enamel that has flowed down over the edge of the casting. They are especially liable to be formed if the trimming is done after the enamel has started to become rigid. Beads are very liable to chip off, since the enamel in them is not only of different thickness from the adjacent enamel, but more especially because the enamel in the beads has been thrown into a condition of strain by the process of trimming. These stresses very frequently do not manifest themselves as chips until some time, often months, after the piece has been made.

REMEDIES.

First. Apply the enamel as thinly as possible at the edges of the piece. This is best done by putting very little enamel on the edge during the application of the first coat of enamel, and only a light coat during the application of the last coat to the whole piece.

Second. If possible, do not heat the ware to the point that the enamel flows down over the edge. This implies that the enamel should be applied to the whole casting in the manner described under Case V.

Third. If trimming is to be done at all, let it be done quickly while the enamel is still soft. It should be done with a good tool and with the blade of the tool making an acute angle with the enameled surface. This gives a clean slanting cut, while

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any attempt to trim with the blade held perpendicular to the surface of the enamel results in more or less beading.

CASE VII. MECHANICAL STRESS IN THE CASTING.

This may be subdivided into three special sub-cases: A, stresses due to the apparent warping and bending; B, stresses due to exterior mechanical restraint; C, stresses which are manifested only by the production of crazing or shivering in the enamel.

A. STRESSES DUE TO APPARENT WARPING AND BENDING.

Many castings, especially those of thin section and long slender shape, show considerable warping and buckling on cooling after the iron is black and the enamel has become fairly rigid. Of course this has a tendency to set up strains between the enamel and iron and in the enamel itself. Such castings are especially common in plants manufacturing specialties. These strains must always tend to produce crazing or shivering and in aggravated cases produce actual rupture.

Remedies.—*First.* Strengthen the sections by the use of iron ribs on the back, etc., so that the tendency to warping and buckling is minimized.

Second. Use a good ground coat and a strong elastic enamel.

B. STRESSES DUE TO EXTERIOR MECHANICAL RESTRAINT.

In making certain styles of castings, especially those for sectional work, it is very important that they conform to a certain shape. The expedient of cooling these castings in forms or clamps is sometimes used. This procedure may so interfere with the normal contraction of the iron and enamel as to set up strains that may cause crazing or shivering. As a case in point, I may quote the following: At a certain plant we were making some rectangular sections about 24 × 48 inches in size. It was necessary that the sides of these sections be perfectly straight for the sections had to be bolted together and make a good butt joint. It was found that when the castings came from the enameling furnace the sides were curved in to a slight extent. When they were cooled in the ordinary way, this curvature was still apparent in the cold pieces. To obviate this difficulty, we rigged up a heavy vice-like affair, clamped the castings in this while

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still hot, and allowed them to cool there. This straightened out the sides and produced a slight bulge at the ends of the piece. The deformation of the ends was immaterial, but we found that this procedure caused the enamel to develop minute crazes at each corner of the section. We concluded that when the castings were cooled in the vice, the ends, which took the stress, were acting like compressed springs. When the clamp was removed the ends of the casting expanded and caused the enamel to craze. Acting on this theory, we decided to put the castings in the clamp, compress them strongly while the iron was still hot and the enamel still plastic, and then to immediately remove the clamps. When we did this, we found that the ends were bulged slightly more than before, that the sides were straight, and that the crazing immediately disappeared.

Another type of stress due to external constraint that enameled iron frequently has to undergo is that caused when a piece of ware that is slightly out of shape has to be drawn into place by bolts when being set up. This, of course, occurs most frequently in sectional ware.

Remedies.—*First.* If possible, so fashion your patterns that the casting will hot have to endure external stress either in cooling or when being put in place.

Second. If stress is to be applied, it should be applied while the iron is still hot and soft and the enamel is plastic.

Third. Use a good ground coat and a strong and elastic enamel.

Fourth. Use a soft ground coat and a soft enamel so that the casting will not have to be heated very hot in the enameling process.

C. HIDDEN STRESSES.

It sometimes happens that crazing or shivering occurs, in certain shaped patterns, for which there is no apparent cause. The defects are not amenable to any of the various treatments already suggested, but disappear when we make certain alterations in the pattern. For this reason we can not but think that the defect is due to strains set up in the enamel or between the enamel and iron, due to some peculiarity in the pattern, the significance of which we do not realize. This type of crazing is the

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most difficult to deal with for it gives absolutely no indication of its cause. We are reduced to depend only on experience and systematic alteration of the pattern. For instance, I have found that, given two sinks of exactly the same size, shape, and thickness, with the exception that one has its outlet near one side or end and the other has its outlet at the center, the latter sink will have decidedly less tendency to develop crazing around the bell than the other. Again, I have found that a kitchen sink with a well rounded bottom is less liable to develop crazing than one with a bottom that is nearly flat. Why these things are so, I can only conjecture. They are merely matters of experience. Similar cases might be multiplied if space permitted. The treatment of each case of crazing or shivering of this sort is a special problem.

Remedies.—*First.* Apply all the rules for general or special crazing that are applicable.

Second. Depend on experience and systematic alteration of the pattern.

CONCLUSIONS FOR PART II.

Crazing in special parts of patterns or in special patterns may be due to a large variety of causes and to various combinations of these causes. Likewise the means of control must be many and varied so as to suit each special case. There is no one "panacea" for crazing in enamels on cast iron. Efficiency in its control depends upon a thorough understanding of the chemical and physical factors involved and on wide experience.

DISCUSSION.

Mr. Landrum: I have had no experience in enameling cast iron, but there is one thing that Professor Staley gave that I do not find is true in the enameled sheet steel industry; that is, that increase of fluorides will increase the brittleness. Now if he wants to say increasing the calcium oxide will increase the brittleness, I will agree with him. One of the best ways to soften an enamel so that it will be less brittle is by an increase of the cryolite without changing your formula; that is, without changing the molecular formula of the batch. This will soften an enamel

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without seeming to change its coefficient of expansion and without making it unsuitable in practice.

These rules that he has given are each very good and agree with my experience so far as the steel industry goes. For practical men, it is well to give directions, for instance, to add flint and to increase the feldspar rather than to increase the silica. We must remember that the cost proposition comes in as a factor when we are making changes in an enamel. It would be much better from the standpoint of cost if a man could figure to put in borax and take out his soda ash, rather than to add boric acid, and this calculation is quite simple.

Prof. Staley: Yesterday there was a discussion as to whether it is the calcium or fluorine of calcium fluoride that makes an enamel brittle. Now, we do not know whether calcium fluoride is converted into calcium oxide in an enamel or what does happen to it, but we do know that increasing the calcium fluoride makes the enamel more brittle. For that reason I put the statement in the form I did.

Mr. Pence: I have had some experience in introducing cryolite into a glaze formula and my experience has been that, preserving the formula the same, cryolite would increase the tendency to craze. I wondered if that was the experience of the enameled iron people. I remember also a citation by some German authority which said the same thing.

Prof. Staley: It is true in cast iron enamel.

Mr. Landrum: I have had a good deal of experience with adding cryolite to enamels. I have taken enamel formulas carrying six or seven per cent. cryolite and increased that cryolite as high as eighteen per cent., and have had enamels every bit as successful as those low in cryolite. None of them craze and none chip under ordinary conditions.

Prof. Staley: There is one difference between sheet steel and cast iron enamel which may explain the fact that Mr. Landrum has been able to use such a large amount of cryolite without getting crazing. I refer to the work of Mayer and Havas. The coefficient of expansion of sheet steel enamels ranges around about twenty-five per cent. less than the coefficient of the sheet steel used, so that there would be very little tendency for his

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enamel to craze. He might add a lot of cryolite and reduce the tendency to shiver and go towards the tendency to craze without really getting into crazing.

Now, the coefficient of expansion of cast iron enamels, by the same figures given by Mayer and Havas for sheet steel enamels, ranges on either side of the coefficient of expansion of cast iron, so in that case we have to be a good deal more careful about the use of substances like cryolite than they do in the sheet steel enamels.

Mr. Bruner: I would like to ask Professor Staley, do you use the molecular formula? If so, where do you put fluorine?

Prof. Staley: I no longer use the formula myself. I have seen a lot of formulae of enamel published and I never saw the fluorine put in. When I read one of those papers it generally takes me about two hours to figure out just what the composition of the enamel was, whether it had any fluorine in it, and how much of the alumina in the formula came from cryolite and how much of it came from feldspar. In writing formulae, it does not make much difference where you put your fluorine; you can put it up in a corner if you want to. I formerly put it between silica and boric oxide; that is just as good a place as any, for we have no right to attach any chemical significance to the position of fluorine in an empirical formula. Putting an expression for fluorine into the formula is simply a means of indicating, in a rather obtuse way, that the enamel contains a certain amount of that element. It also aids us in calculating the actual batch of the enamel.

Mr. Landrum: I have done some interesting work on the analysis of fluorine in glazes, and I find that in ground coat enamels for sheet steel, where the frits are properly fused, the fluorine from the calcium fluoride entirely disappears. In white enamels, however, when cryolite is added as an opacifier, the melting is not carried so far, and fluorine does remain in the enamel. If the melting is carried far enough to drive out all of the fluorine, the white opacity also disappears. In white enamels for sheet steel, properly smelted, about twenty per cent. of the weight of the cryolite is given off as silicon fluoride, and in figuring for

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this loss, I consider that cryolite loses twenty per cent. of its weight in smelting.

Mr. Bruner: Twenty per cent. of the fluorine or cryolite?

Mr. Landrum: Twenty per cent. of the cryolite. I figure twenty per cent. loss as fluorine.

Mr. Bruner: What is the total percentage of fluorine?

Mr. Landrum: I think it is more than fifty per cent.

Prof. Staley: It has been shown in analyses by the Germans that if you frit the enamels as we frit them in the cast iron industry, that is, run your frit through the kiln in one to two and a half hours and apply it in an oxidizing atmosphere, there is a lot of fluorine left in the enamel.

NOTE PREPARED AFTER READING THE PAPER.

Mr. Blackham: To my mind this paper covers the ground thoroughly in a plain, practical manner, treating conditions as they actually exist, not theories.

Supplementary to "Thick Spots," I have found it necessary in some cases to thicken up the pattern in some particular spot. I have in mind an 18″ × 30″ flat rimmed sink pattern of which we were working two, made from the same master pattern and filed in exactly the same manner. The casting from one of these patterns crazed in the corner, at the rim. I tried making it thinner; this only seemed to aggravate the difficulty. The pattern was then made very heavy at this point, and gave no further trouble. The other pattern, with apparently the same condition, gave no trouble at this point.

When "lifting" occurs, my experience has been that it usually can be traced to the slush coat. Either the slush coat is defective, deficient, overheated, or applied too thin. Lifting will occur on thin spots in castings, due to the slush coat being burned off at this point.

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SOME PROBLEMS ENCOUNTERED IN PRODUCING A STIFF-MUD FLOOR TILE.

By W. H. GORSLINE, Rochester, N. Y.

Quarry tiles appear to most clay workers to be about as simple a product as can be manufactured from clay—a rectangular slab, of not large enough dimensions to make its handling difficult, and with enough thickness to reduce warpage to a small factor. It has been the experience of the writer that their manufacture is not so simple as it looks, a conclusion which the experience of others will probably reinforce.

The object of this note is to describe some of the problems encountered in taking up the manufacture of quarry tiles. The work was undertaken as a side-line in a factory which had been manufacturing another line of ware for many years, and in which all adjustment for the success of the staple product had been pretty fully worked out long ago. Hence, there was a tendency to view the requirements of the new line in the light of the regular routine of the old line, which probably hindered to some extent the early attainment of success.

When the line was once launched on the market, production had to be crowded; this limited us to experiments undertaken only as a means to an end, and not for the purpose of establishing or proving general laws. Possibly most of the devices and experiments used are old and may be known to experienced clay-workers; but they certainly are not known to all. For in our efforts to overcome our defective wares, we sought the experience of others; and, in most cases, we could not obtain the aid needed and had to work the matter out for ourselves. Some of these points were very simple, yet they made the difference between good and bad ware, between success and failure.

By setting forth his own experiences, the writer hopes to induce others to record theirs, with a view to accumulating more complete and exact information.

Most companies depend upon the knowledge their men have accumulated and never gather it together and analyze it. When the latter is done conflicting views are sure to develop. In the end, such study leads to efficiency and better results. Meetings between foremen and managers are productive of much good,

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and the ideas advanced in this way can be tried out with the certainty of the interest and, generally, the hearty support of the men.

The studies of the writer were devoted chiefly to three separate problems. First, making a mechanically perfect ware in the green state; and, second, placing it in the kiln in such a position that it would remain true and square, and of good color after burning; and third, the proper method of burning.

MANUFACTURE OF THE WARE.

The Clay.—The clay used was the same that had been in use for a number of years in the plant. It was made up of a mixture of two local surface clays with a New Jersey fire clay, the whole forming a very plastic body. The structure resulting from flow through the dies, therefore, gave trouble, probably far more trouble than would have been the case with ordinary fire clays or shales.

The Tempering.—The clays were ground and tempered in wet pans, with four mullers of serpentine tread for each pan. This system produced clay of excellent physical structure.

The First Manufacture.—For the first year or so, a small quantity of tile was made, using a piston press with vertical delivery. To the bottom of the press was attached a die which made a rectangular tube of clay, scored at the corners, so that on breaking up each block made four tiles. This method had two difficulties which condemned it: first, the clay bar had a surface skin, beneath which air bubbles were formed; second, the die was not lubricated, which made it impossible to produce square corners without repressing the blanks (see Fig. 1).

The scoring of the square tube had to be deep enough to permit the men to separate the tile while still green; and, if scored deeply enough to allow this to be done without injuring the tile, the hollow column was found to be not strong enough to support its weight in a horizontal position, and the top quarter collapsed.

To eliminate the first objection recited, as well as to avoid the disadvantages of repressing, a small auger machine and cutting tables were procured, and lubricated dies were designed to make 4″ x 4″ and 6″ x 6″ tiles, producing a square tube to be cut

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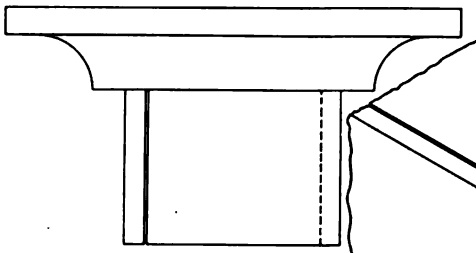

FIG. 1

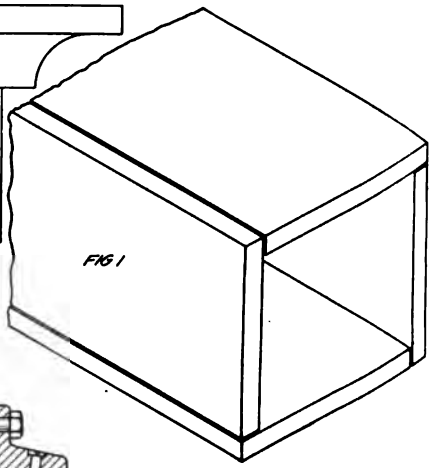

FIG. 1

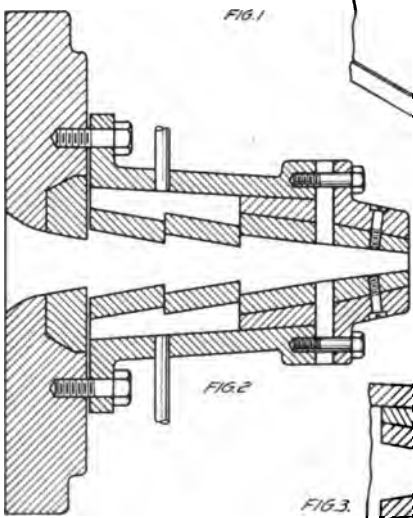

FIG. 2

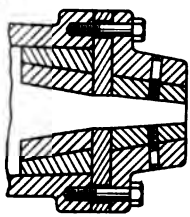

FIG. 3.

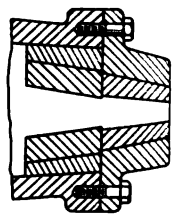

FIG. 4.

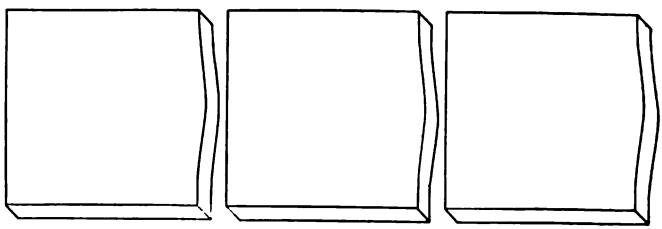

FIG. 5.

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into four tiles at a time, like the original method. It was thought too difficult to make 9″ x 9″ tiles horizontally in this way, and a die making a single column of clay 9″ wide and $1^{3}/_{4}$″ thick, plus shrinkage, was procured for this size. The latter die proved to be the best.

Making a Smooth Clay Bar.—These three original dies for the auger machine were made with an open space, between the slicker and the scale next to it. The expectation in this was that surplus lubrication and slush would work out through this opening and the column passing through the slicker would be free from defects from these causes (see Fig. 2).

In spite of painstaking efforts, the contrary was the result, and these dies with openings never gave satisfaction. Particles of grog would become caught in the opening and mar the surface of the clay; slush would accumulate there and eventually soften up the clay or run over on to the surface; often the clay would catch on the edges of the slicker and the column. Sometimes the clay would even back up out of these openings. All of these difficulties happened in spite of careful tempering.

To eliminate the objections attributed to the opening between the slicker and the first scale in the original dies, the opening was closed up by inserting blocks of wood. The wood fitted fairly accurately and extended almost through to the clay. The result of this change was a decided improvement as regards excess water, slush, etc., although some trouble with water in a lesser degree continued until we learned how to adjust the exhaust pipe better.

Encouraged by this experiment, we inserted a metal piece to close up the opening; this piece was machined nicely to fit to the discharge end of the last scale and to the receiving end of the slicker, forming an almost straight line between these two points as shown in Fig. 3. This arrangement gave the smoothest column yet produced and was adopted for the time, subject to further trial.

In the meantime, it was decided that the dies making a square tube must be abandoned, for the reasons given above, and a new six inch die was now designed to make a single stream bar in

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the same way as the nine inch die; the new four inch die designed at the same time was similar, but gave a column eight inches in width, the column being split as it issued from the die by a piece of wire stretched vertically across the die, back of the slicker.

The chief difficulty now seemed to be marring and "feathering" of the surface, which recurred frequently and which was not controlled by the re-built dies.

The holes for the bolts by which the slicker was held to the scale box were large enough to permit of some adjustment, and as we were trying everything at this time, one day we bolted the slicker on as high up as possible, giving an offset in the line from the last scale. Such a good surface on the bar was the result of this adjustment that we continued changes along this line and finally proved to ourselves that this offset was an absolute essential to the production of a smooth bar of clay. The clay was allowed to expand and some moisture to accumulate at this point, the latter aiding the slicker in smoothing the column as it passed through. Marring was now entirely overcome (see Fig. 4).

At first the dies were made so that the offset was at the top only. Later on it was proven that to have a slicker with the receiving end larger in all directions than the last scale was the best arrangement. This stopped roughing up the sides of the column, as well as the top, and had a tendency to give a drier bottom. With these dies, it was found that a slicker from $^1/_{16}''$ to $^1/_8''$ larger at receiving end than the scale next to it was the best proportion, and it was soon possible in this way to secure a column of clay with perfectly smooth surface and edges at times. Of course, the slicker must taper to the discharge end, at which point the opening should be the smallest in the die.

The First Scales.—The scales in these dies were independent of each other, coming together with butt joints. Lubrication was provided for by placing thin strips of tin between the joints, at first; but later it was found that the tin was unnecessary. The pipe connection on the lower side of the die took away surplus steam and condensed water which accumulated in the jacket space, and which would otherwise squirt forth at times, ruining the surface of the column.

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PRODUCING SQUARE TILES.

Operating as above for a time, the fact was disclosed that after drying, one wire cut edge of the tile was no longer straight. Although the tile, if carefully squared up immediately after cutting, appeared almost straight where cut and accurate enough for this class of material, it was found that after drying one end still remained fairly straight where cut and the other end was very much bowed or convex. The convex end was the forward cut of the tile, farthest away from the machine (see Fig. 5).

There was no concavity at the back end of the tile to correspond with the convex cut at the front end; or, in other words, one end was almost straight and the other end was bowed. This peculiarity was a puzzle for everybody at first, and various explanations were put forth.

Upon analysis, it seemed to be due to a differential flow of the clay in the die. The outside portions of the column were held back by the sides and corners of the die more than the center, which permitted the central portion of the column to flow relatively more freely. If examined immediately after coming from the cutting table, this defect was generally not noticeable; but after the clay began to dry and relax, the bowed end appeared; sometimes the deflection from a straight line was as much out at the farthest point as $^{3}/_{16}''$. It seemed necessary to get at this defect by changing the contour of the interior of the die, stopping this unequal flow of the clay. Eventually, this was accomplished in the following way:

The receiving side of hinge plate was machined to flare out at the sides and corners of the opening as much as possible, so as to offer the least resistance to the clay as it entered at these points (see Fig. 6, heavy lines only). This proved not to be enough, and the dies were re-built about as shown by the other line in Fig. 6, with the opening in the center contracted to retard the flow of the clay, where it formerly ran the freest. This contraction of the opening at the center was relieved and gradually increased towards both sides, so that after some experimenting a contour of such proportions was adopted as to prevent uneven flow and give a tile, which, after drying, was square at both ends.

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This idea was carried so far in one of our experiments that a concave end was produced in place of the convex.

"Dished" Tile.—When the cause of bowed ends was understood and the trouble corrected, a new difficulty developed as a direct result of the remedy applied. The central portion of the face of the column was lower than the outside portions, due to the lines of the interior of the die.

The tiles made from such a die were dished in the center. The cause was soon apparent, but the retarding lines of the dies could not be relieved for fear that the old trouble of bowed ends would reappear. Hence, we resorted to an expedient which the writer has since learned is sometimes used in the brick business, but which was suggested by reading an English book, "The Manufacture of Roofing Tiles," by A. T. Ackworth.

The portion of the slicker which formed the top surface of the column was machined out about as much as the column of the clay was depressed in the center and along lines approximating the form of the depression. The top face of the slicker was concaved in a manner somewhat like the concavity on the face of the column. This gave the clay a chance, when it reached the slicker, to expand in the center where it had been depressed by the scales. After a little adjusting, this made possible a column quite flat and level on the surface, and which dried square when cut square (see Fig. 7).

Blisters.—A considerable number of blisters were generally present in the smooth surfaced bars produced on the single stream dies. These were reduced by keeping the barrel of the machine at all times as nearly full of clay as possible, so as to work out the air.

Several times the question of the effect produced by varying the distance between the auger and the die arose. Originally the die was bolted on to a hinge plate, hung directly on the auger machine in the customary manner, which gave only a space of three inches from the end of the auger to the opening of the die.

Thus the influence of the auger was partly responsible for imperfect moulding of the clay, and for a tendency of the column to run more in one direction than another. It was found by

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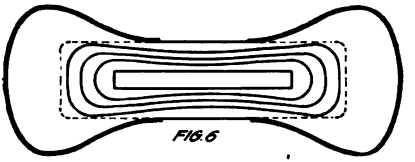

FIG. 6.

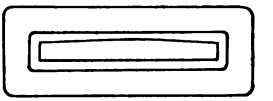

FIG. 7.

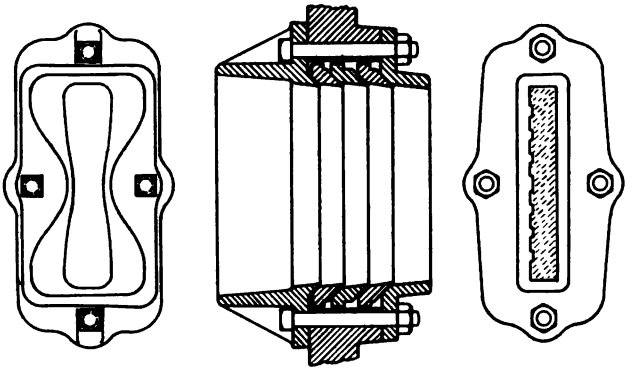

FIG. 8.

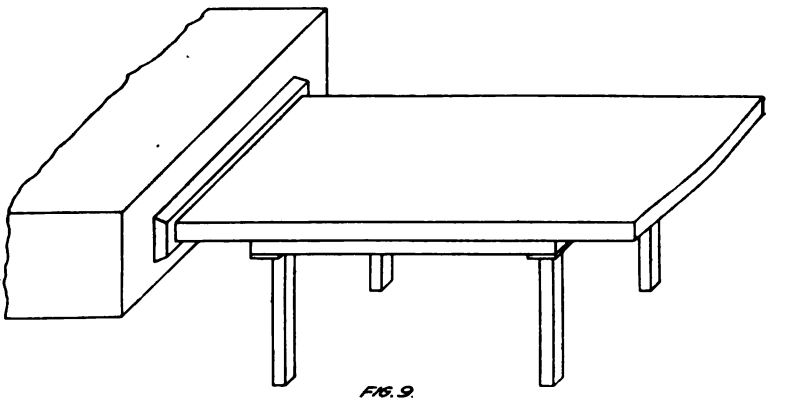

FIG. 9.

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increasing this distance and forming an intermediate collection chamber, a more even flow of the clay was secured and more air was worked out. This resulted in a column which had less blisters on the surface and less lamination in the body.

At one time, the distance was increased to 12 inches more than it originally was, making altogether 15 inches, but it was found this placed too great a duty on the small auger machine, and retarded the flow of the clay too much. Very satisfactory results eventually were secured by operating with a distance of 9 inches from the end of the auger to the opening of the die. On special wares like floor and roofing tile, a double auger machine recommends itself.

Die Linings and Lubrication.—In changing the dies and rebuilding them, as described in the foregoing, the linings finally adopted were of the telescopic variety, the snout of one ring entering into the base of the ring just ahead. This system prevents any movements of the scales and makes it possible to control the amount of lubrication by regulating the tightness with which they are screwed up. The lubrication can also be distributed with some uniformity. The results are usually more satisfactory than with the butt-joint type of scale. If a die can be constructed so that there is ample lubrication between the first two scales nearest the machine, there is not so much lubrication needed throughout the rest of the die (see Fig. 8).

Steam seemed, in this case, to be the best form of lubrication, because it could be more easily controlled. When stopping during a run, the steam never made the clay excessively wet and sloppy, as water did. This might not be the case where less pressure was required.

With the clay and the die arrangements described, a pressure of not less than 28 pounds to the square inch gave the most satisfactory results. This was provided by tapping on to a steam line and running the pipe into a receiving tank, from which the steam was conveyed by means of a small pipe to a point near the die. From there on a steam hose was used, to give the flexibility and convenience desirable in changing dies. In the line leading to the receiving tank, was placed a reducing valve, to regulate the pressure: on the receiving tank was fitted a steam

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gauge. The latter showed at all times the pressure which was being used, and the former readily permitted variations in pressure.

Speed of Flow through the Die.—When originally installed, the auger machine was run at a speed specified by the manufacturers: this turned out the bar faster than the men could handle it, and it was found that at a reduced speed a better class of ware was produced. The conclusion seems justified that with this class of ware, in order to secure a good well moulded product, the machine should be operated at less than its maximum capacity.

The actual capacity of the machine, as is well known, varies with different clays and may be below or above its rated capacity. It is the writer's opinion that with some clays too great speed is objectionable with ware like floor and roof tile, where the thickness of the bar is much less than that of brick. Considerable compression of the clay is required to force it from the barrel of the machine through the slicker of the die. This cannot be accomplished and the necessary quality maintained, if running too fast.

Exterior Resistance.—During the experiments conducted in trying to reduce the bowing of the tile, there was installed a wooden table between the die and the cutting table, leveled to correspond with the bottom of the column, over which the column of clay had to be forced before it came to the rollers on the cutting table. The purpose of this was to overcome some of the stretching effect and mould the clay better. This board we named the "resistance board," for lack of a better name (see Fig. 9).

If 20″ or 24″ long, this resistance board requires rollers running in oil to slightly lubricate the bottom of the column, as otherwise the latter sticks to the board, and soon so much slush accumulates that the machine has to be stopped and the board cleaned.

Another advantage of this board, in the case in hand, was the space it afforded between the die and cutting table, in which the column could be inspected. A man could stand with a trowel and prick and rub out the blisters, and remove foreign particles from the clay.

Shape of Dies.—Dies should taper from the receiving end

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to the discharging end, including the slicker, which should not be straight at any point. A straight slicker constantly gave trouble, and roughed the surface of the column, producing a feathery effect on the surface or on the edges. The same defects will also be produced if the receiving end of the slicker is not larger than the scale next to it.

The internal angles and edges of the die should be rounding, the maximum radii being at the entrance end of the die and reducing gradually throughout the die until the square form of the finished tile is produced at the discharge end of the slicker.

There is an opportunity to do some experimenting to determine the principle governing the proper length of dies, and the relation of the taper to the length. The writer has not had enough experience along this line to go on record, but definite data on this subject are a much needed addition to ceramic records.

Weathered Clay.—Weathered clay is far more satisfactory for ware of this character and reduces die troubles, air bubbles, lamination and warping.

BURNING.

The tiles were set in the kiln singly on benches close together, after the manner of setting roofing tiles. There were several reasons for this:

First, the clay would not safely sustain the weight of setting the tiles one upon another throughout the kiln.

Second, color effects sought could best be secured in this way.

Also, in taking the tiles from the cutting table they were faced up, in stacks, which reduced the quantity of warped tile, and forced most of the drying to take place from the sides and backs, thereby reducing the tendency towards the formation of air bubbles and blisters and scum on the surface while drying.

In burning, a system had been developed a few years before which gave most satisfactory results and which, with a few changes, we were able to use in burning quarry tile. The absence of a fixed system or schedule for burning is to be deplored, because the tendency with most burners, when a kiln does not come up to the mark, is to alter their method in the next kiln, without stopping to consider whether they have followed the system in

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the past burn. With a schedule in use which only allows them a little practical latitude, if a kiln does not come out just right, it is easy to prove in the majority of cases that the poor results are due to some departure on the part of the burners from the schedule.

The tiles in consideration were burned under a fixed schedule. The average burn was about 22 hours for water-smoking, 70 hours for the oxidation period, and 40 hours for the vitrification period, averaging about 132 hours to reach the maximum temperature of 1165° C. Up to 900° C., an excess of air was allowed to enter into the kiln, to accomplish the process of oxidation. The maximum temperature was reached twelve to fifteen hours before firing stopped. This time for soaking at full heat insured a uniformity of burning throughout the kiln, and, with this clay, generally removed whatever scum was liable to form on the tiles in the parts of the kiln where the circulation was poor.

Quarry tiles, like paving brick, should be as tough as possible, on account of the wear on their surface. To accomplish this, cooling was always done slowly with the aim of producing a cooling curve that approximates the heating curve in duration and rate of change.

In conclusion, many thanks are due to E. M. Freese & Co. for painstaking assistance rendered during the experimental work on dies which is reported in the preceding notes.

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OILS, FATS AND GREASES FOR DIE GREASING IN THE MANUFACTURE OF DUST-PRESSED WARE.

By GEO. SIMCOE and A. F. SMITH, Trenton, N. J.

The object of this investigation was to secure accurate data concerning various oils, fats and greases and, if possible, show any preference, other than cheapness, in their selection for die greasing in the manufacture of various dust-pressed products.

The outline of the work is as follows:

First. To show the physics of the part played by oils, etc., upon dies in making dust-pressed ware.

Second. List of all commercially available oils, fats, greases, waxes, pigments and metal filings.

Third. Securing samples of materials described above.

Fourth. Test to show harmful effect, if any, of the various members of above list in raw state upon both burned and unburned clay products.

Fifth. The selection of a proper cutting oil.

Sixth. Testing under practical conditions of various materials on the list combined with kerosene, and showing the relative cost of working mixtures.

Seventh. Some old ideas and practices.

Eighth. General conclusions.

First.—Oil is applied to a die in one of two ways: either directly with a brush, or indirectly by mixing the oil in the clay. In the latter method when pressure is applied, the oil is forced in a thin film over the die. In either case, the ultimate condition is practically the same. The popular term for this process is "die lubrication," which seems to be wrong, for the function performed by the oil is not lubrication, as the following short definition will show: "Lubrication has for its object the reduction of friction." While there is undoubtedly friction developed between die and clay, the oil is not there to reduce that. Who would say "lubricate" the frying pan? Absurd! You would say "grease" it, so that a film of grease may interpose between the fried egg and the pan to prevent sticking. We claim the film of oil between die and clay is analogous, and therefore believe we are right in saying oil, etc., for "greasing" dies.

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The physics of the proposition may be considered from two standpoints:

(1) The oil prevents the adhesion between die and clay.

(2) Where there is a tendency to form a vacuum, the oil being made up of minute elastic globules, which under pressure form more or less continuous film between die and clay but when pressure is removed become rounded again, what was a continuous film becomes full of inter-globular canals through which air may pass and relieve what is commonly known as the "suck."

Second.—After consideration of between 400 and 500 oils, fats, waxes, etc., those given in Table I were selected as commercially available, and in addition to these a number of color pigments and metal filings such as might be found in a pottery with a view to showing that if spots or discolorations were found they might be traced from their characteristic coloring or discoloring effect to foreign matter in the oil.

TABLE I.—LIST OF OILS, FATS, GREASES, ETC.

Oils				
Class	No.	Name	Specific gravity	Cost per gallon
Animal	1	Neats foot	0.9169	$0.85
	2	Lard oil	0.9400	0.80
	2A	Rancid lard oil	...	0.75
	3	Tallow oil	...	0.75
Fish	4	Brown fish	0.9334	0.65
	5	Sperm oil	...	0.95
	6	Seal oil	...	0.65
Vegetable Drying	7	Linseed	0.9350	0.98
	8	Hemp seed	0.9280	0.85
	9	Soya bean	0.9270	0.65
Vegetable Semi-drying	10	Cottonseed	0.9306	0.62
	11	Castor	0.9591	1.25
	12	Peanut	...	0.70
Vegetable Non-drying	13	Rape seed	0.9139	0.85
	14	Mustard seed	0.9170	0.80
	15	Olive	0.9100	0.95
	16	Maize	0.9274	0.65
	17	China wood	...	0.60
Essential	18	Turpentine	0.8727	0.60

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TABLE I (*Continued*).

Class	No.	Name	Specific gravity	Cost per gallon
		Waxes		
Mineral	19	Crude petroleum	...	0.09
	19A	Texas crude oil	...	0.09
	20	Paraffine oil	...	0.18
	21	Cylinder oil	...	0.40
	22	Engine oil	...	0.25
	23	Gasoline	...	0.12
	24	Benzine	...	0.06
	25	Kerosene	...	0.06
	26	Mineral sperm	...	0.12
	27	Spindle oil	...	0.15
	27A	Roof pitch	...	0.80
	27C	Pitch	...	0.80
	27E	Residuum	...	0.09
Vegetable	28	Carnauba	0.9990	1.20
Animal	29	Beeswax	0.9627	3.38
	30	Spermaceti	0.9600	1.50
Mineral	31	Parowax	...	0.75
	31A	Mineral wax	...	1.73
		Gums		
	32	Caoutchouc	...	2.40
Vegetable	33	Gum arabic	...	1.60
	34	Gum tragacanth	...	5.40
Animal	35	Gelatine	...	1.88
Mineral	35A	Mineral gelatine	...	0.35
Fish	36	Isinglass	...	4.55
		Fats		
	37	Palm oil	0.9209	0.75
Vegetable	38	Cocoa nut oil	0.9259	0.90
	39	Japan wax	0.9840	1.13
Animal	40	Tallow	0.7940	0.60
Mineral	41	Petrolatum	...	0.23
		Greases		
Animal	42	Butter	...	2.25
	43	Pure lard	...	1.20
	44	Commercial pure lard	...	0.90
	45	Compound lard	...	0.68
	46	Beef stearine	...	0.98
	47	Mutton stearine	...	1.05
	48	De gras	...	0.20

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TABLE I (*Continued*).

Other Compound Commercial Oils

No.	Name		Price per gallon
100	O. F. Zurn Co.	Orient die oil	$0.40
101	O. F. Zurn Co.	Die oil	0.40
102	O. F. Zurn Co.	Castor compound	0.40
103	O. F. Zurn Co.	Lustre oil	0.40
104	O. F. Zurn Co.	Press oil	0.18
105	Crew-Levick Co.	Compound lard oil	0.40
106	Crew-Levick Co.	Pump oil	0.15
107	Crew-Levick Co.	Press oil	0.18
108	Crew-Levick Co.	Acme mould oil "A"	0.31
109	Crew-Levick Co.	Acme mould oil "B"	0.29
110	Crew-Levick Co.	Acme mould oil "C"	0.35
111	Crew-Levick Co.	Acme mould oil "D"	0.285
112	Crew-Levick Co.	Acme mould oil "E"	0.255
113	Crew-Levick Co.	Acme mould oil "F"	0.235
114	Glycerine		3.00
114A	Mineral castor oil		0.18

Pigments and Metallic Filings.

115	Pure graphite	Samples tested for color effect only
115A	Metallic zinc	
116	Manganese dioxide	
117	Green oxide of chromium	
118	Chromate of iron	
119	Copper oxide	
120	Cobalt oxide	
121	Copper filings	
122	Iron filings	
123	Brass filings	
124	Babbitt metal filings	
125	White brass filings	
126	Zinc filings	

Third.—Securing samples of materials described in above list required about six months, as experimental quantities are much more difficult to obtain than barrel lots. In order to have a record for reference test, a small sample of each material used was taken and placed in a homeopathic vial and numbered in accordance with the list.

Fourth.—A test was made to show harmful effect, if any,

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of various members of above list in raw state upon the burned and unburned clay products. For this test, we made a number of small disks of red and white burning bodies about $1^5/_8$" in diameter by $^1/_4$" thick. A small quantity of each material was applied to the samples, the white being glazed after applying the oil, and the red left unglazed. Two sets of the white samples were fired, one at cone 12 and the other at cone 3. The two sets of red samples were fired at cones 6 and 3 respectively.

An examination of the fired samples shows that the oils, fats, waxes, gums and even pure graphite do not leave any specks, but the pigments and metal filings give their characteristic color, as was to be expected. When it is considered that the oils, fats, waxes and gums are hydrocarbons, it is not surprising that they are burned out completely at the temperature to which ceramic products are fired.

The accompanying cut gives a very good idea of the burning points of various oils.

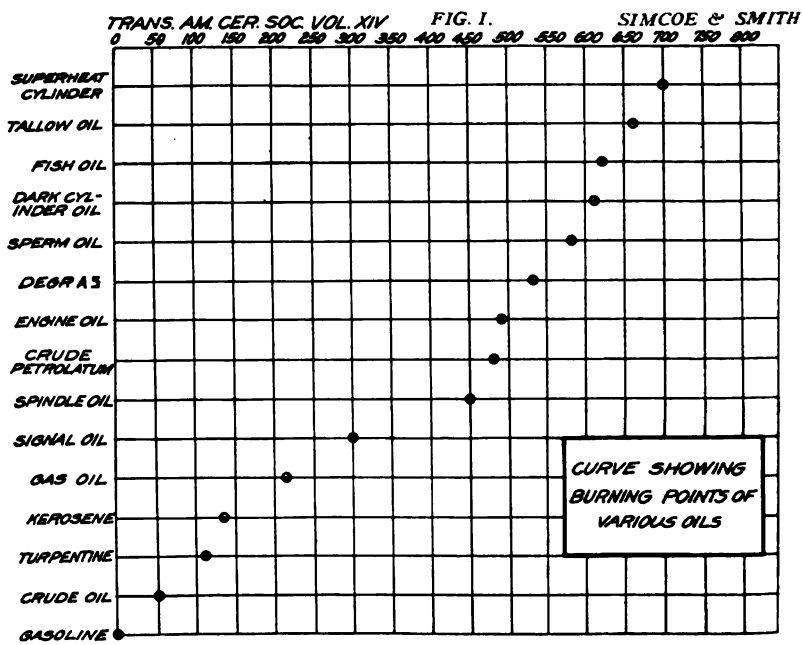

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CHART OF THE DISTILLATION OF PETROLEUM.

Number of distillate	Description of distillate
First	Gas.
Second	Liquids of specific gravities of 75° to 95° Bé. commonly known as "gasoline."
Third	Liquids of specific gravities of 58° to 68° Bé. known as "benzines." Are volatile.
Fourth	Liquids of specific gravities of 55° to 60° Bé. All flash below 59° F.
Fifth	Liquids of specific gravities 42° to 55° Bé. The 42° material flashes at 172° F.

After this, a heavier oil under 40° Bé. remains in the still. This is treated by some refiners by filtration, and oils known as spindle oils, red oils, or light machinery oils are produced. These all have a flash test below 450 to 475° F. The residue of heavy material left in the still is treated and converted into cylinder stocks used for making heavy bodied cylinder oils of various grades. These all flash below 600° F.

The point we wish to bring out is that all oils obtained from crude oil are vaporized or volatilized below 650° F.

Fifth.—The selection of a proper cutting oil. Having proved to our own satisfaction that there was nothing to prevent the use of any of the materials in Table I, so far as causing discoloration was concerned, excepting, of course, the pigments and metal filings, we proceeded to look up the best and cheapest cutting oil to combine with them. Gasoline and lighter oils than kerosene were tried, but were more expensive as well as dangerous. We even tried water as a cutting agent, forming emulsions with straight oils and in direct combination with saponified oil, as "castor compound," No. 102 in the list. But water will not work, as it combines with the clay, makes it sticky, and is really worse than nothing on a die. Therefore, on account of cheapness, general good working qualities, and reasonable safety in working and storage, we decided to use kerosene.

Sixth.—Preparation and testing under practical conditions of oils, fats, waxes and gums of Table I combined with kerosene to show relative cost of working mixtures.

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In preparing our samples for testing, we started with 20 parts kerosene to 1 part oil or grease to be tested. Measuring carefully in a 120 cc. graduate, we aimed to make a uniform batch of 100 cc. After making up the samples as described, they were tried out under practical dust-pressing conditions; and in order that the results might be as uniform as possible, the same man did all the pressing and the same dies and presses were used on the sample body, and these conditions were maintained throughout the test.

The body used was an electric porcelain body maturing at cone 12, containing no whiting and composed of spar, flint, Florida clay and English china clay. The size and shape of the ware pressed were of such character as to give a fair test, being of the types used in electric porcelain. Fig. 2 shows detail of same.

Fig. 2.

If the oil sample worked at 20 to 1, a new sample was made increasing the ratio, and conversely if it would not work. The ratio of kerosene to oil was decreased or increased until the working combination was found or it was plain that it would not work.

Table II shows the results of this work from which a rough idea can be had of the relative cost of the ultimate mixture.

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TABLE II.—THE KEROSENE COMBINING TABLE.

No.	Name	Price per gal.	Mixed with parts kerosene at 6c. per gal.	Working value	Cost of mix per gallon
1	Neats foot	0.85	20	O. K.	0.098
2	Lard oil	0.80	20	O. K.	0.095
2A	Rancid lard oil	0.75	20	O. K.	0.093
3	Tallow oil	0.75	20	O. K.	0.093
4	Brown fish	0.65	20	O. K.	0.088
5	Sperm	0.95	20	O. K.	0.103
6	Seal	0.65	15	O. K.	0.097
7	Linseed	0.98	15	O. K.	0.118
8	Hemp seed	0.85	20	O. K.	0.098
9	Soya bean	0.65	20	O. K.	0.088
10	Cottonseed	0.62	10	O. K.	0.111
11	Castor	1.25	30	O. K.	0.098
12	Peanut	0.70	18	O. K.	0.093
13	Rape seed	0.85	20	O. K.	0.098
14	Mustard seed	0.80	15	O. K.	0.106
15	Olive	0.95	15	O. K.	0.116
16	Maize	0.65	15	O. K.	0.097
17	China wood	0.60	15	O. K.	0.094
18	Turpentine	0.60	1	N. G.	...
19	Crude petroleum	0.09	1	N. G.	...
19A	Texas crude oil	0.09	1	N. G.	...
20	Paraffine oil	0.18	1	N. G.	...
21	Cylinder oil	0.40	1	N. G.	...
22	Engine oil	0.25	1	N. G.	...
23	Gasoline	0.12	1	N. G.	...
24	Benzine	0.06	1	N. G.	...
25	Kerosene	0.06	1	N. G.	...
26	Mineral sperm	0.12	1	N. G.	...
27	Spindle oil	0.15	2	O. K.	0.090
27A	Roof pitch	0.80	1	N. G.	...
27C	Pitch	0.80	1	N. G.	...
27E	Residuum	0.09	1	N. G.	...
28	Carnauba	1.20	1	N. G.	...
29	Beeswax	3.38	10	O. K.	0.362
30	Spermaceti	1.50	1	N. G.	...
31	Parowax	0.75	1	N. G.	...
31A	Mineral wax	1.73	10	O. K.	0.212
32	Caoutchouc	2.40	1	N. G.	...

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TABLE II (*Continued*).

No.	Name	Price per gal.	Mixed with parts kerosene at 6c. per gal.	Working value	Cost of mix per gallon
33	Gum arabic	1.60	1	N. G. (S)	...
34	Gum tragacanth	5.40	1	N. G. (S)	...
35	Gelatine	1.88	1	N. G. (S)	...
35A	Mineral gelatine	0.35	100	O. K.	0.063
36	Isinglass	4.55	1	N. G.	...
37	Palm oil	0.75	50	O. K.	0.074
38	Cocoa nut oil	0.90	5	O. K.	0.200
39	Japan wax	1.13	1	N. G.	...
40	Tallow	0.60	35	O. K. (S)	0.075
41	Petrolatum	0.23	8	O. K. (S)	0.079
42	Butter	2.25	5	O. K. (S)	0.425
43	Pure lard	1.20	2	O. K. (S)	0.440
44	Commercial pure lard	0.90	5	O. K. (S)	0.200
45	Compound lard	0.68	1	N. G. (S)	...
46	Beef stearine	0.98	1	N. G. (S)	...
47	Mutton stearine	1.05	1	N. G. (S)	...
48	Degras	0.20	50	O. K.	0.063
100	Z orient die oil	0.40	30	O. K.	0.071
101	Z die oil	0.40	30	O. K.	0.071
102	Z castor compound	0.40	1	N. G.	...
103	Z lustre oil	0.40	25	O. K.	0.073
104	Z press oil	0.18	10	O. K.	0.071
105	C–L compound lard oil	0.40	20	O. K.	0.076
106	C–L pump oil	0.15	10	O. K.	0.068
107	C–L press oil	0.18	10	O. K.	0.071
108	C–L acme mould oil "A"	0.31	15	O. K.	0.076
109	C–L acme mould oil "B"	0.29	20	O. K.	0.071
110	C–L acme mould oil "C"	0.35	20	O. K.	0.074
111	C–L acme mould oil "D"	0.28½	20	O. K.	0.071
112	C–L acme mould oil "E"	0.25½	15	O. K.	0.072
113	C–L acme mould oil "F"	0.23½	15	O. K.	0.071
114	Glycerine	3.00	18	O. K.	0.215
114A	Mineral castor oil	0.18	15	O. K.	0.067
115 to 126	Samples tested for color effect only.				

O. K. Works all right. N. G. Will not work. (S). Settles.

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Seventh.—Some old ideas and practices.

PLASTIC BODY.—We learned that some potters claimed that certain oils would not work on their ware, because it was too rich. Assuming that the richness came from ball clay, we made up a body containing 30 per cent. ball clay and made several comparative tests, and found that the ball clay body, being stronger and holding together better, did not require so strong an oil mix, *i. e.*, a mix containing proportionately higher content of kerosene could be used.

SHORT BODY.—Another instance was brought to our attention where a factory had a body that they claimed could not be worked with lard or refined neatsfoot, but that a low grade of neatsfoot oil, heavy in foots, probably adulterated with horse oil, would work satisfactorily. We were able to get hold of a sample of this body, and found it to be very short and we were not sure whether the shortness resulted from lack of plastic clay or from the presence of whiting. However, we tried this body and found that it would work with lard oil, compound lard oil, etc., only using the mix stronger than shown in the foregoing table. To make sure that whiting would not produce any complications, we made up a body containing 3 per cent. whiting and the result was a short body that had the characteristic oil requirements of the body last mentioned. This bears out our work when preparing the paper on "Dust-Pressed Ware" for Vol. XII. We found then as now that plastic bodies do not require as rich an oil as do short ones.

CAMPHORATED OIL.—Many factory peculiarities and practices were brought to our attention, such as the use of camphorated oil successfully where all others failed. Now, camphorated oil is nothing more than olive oil and gum camphor—that is, it should be, but the chances are that what was used was cottonseed oil and gum camphor which is the common substitute.

VISCOSITY THE CHIEF REQUIREMENT.—From our experience, we feel that there must have been some simple explanation of the proposition. For instance, the degree of viscosity seems to be a factor in our work (see mineral gelatine in table). No doubt, if the proper consistency of their regular oil had been

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secured, they would have experienced no difficulty. It was to explore this field that gums and waxes were considered in the table but, as you will note, with no apparent good results.

GUM TO PREVENT OIL SETTLING.—Another point that might be worth mentioning is that based on the potter's idea of using plastic clay or gums to hold up his body or glaze. We tried using gums, etc., to try to make such oil mixes as would stay up, but our results were negative.

TURPENTINE.—Some instances are known of using turpentine for die greasing where a plastic body was used, whether due to the drying qualities of turpentine we do not know, as we do not handle the plastic proposition. It may have been used in connection with a heated die.

VALUE OF WORK.—Pages might be written on these various shop practices, but enough has been shown to convince the reader that there is great need of light on the subject. However, we believe that having exploded the idea of black spots, etc., coming from oil high in carbon, the potter has only to consider the "Kerosene Table" and select his cheapest material. A consideration of the table shows that de gras and mineral gelatine are the cheapest. De gras is a thick grease recovered from leather, wool, etc., after partial saponification and then returning to oil again. Mineral gelatine is obtained by treating a soap which is a potassium or sodium stearate with aluminum sulphate and after a complex reaction aluminum stearate and potassium or sodium sulphates are formed.

While these materials are easily obtainable, the proposition of mixing them with kerosene is somewhat troublesome to the average potter, as they would have to be mixed with kerosene and heated to secure an even mix. However, a much better way is to take up the matter with your oil man, and get him to sell you a compound oil made of a cheap spindle oil and either de gras or mineral gelatine. This will give you a cheap heavy oil that you will be able to mix with your kerosene in the same manner as you mix lard or neatsfoot oil.

Eighth. General Conclusions.—As a result of our work, we claim the following:

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a. A knowledge of the commercially available oils, etc.

b. The value of such oils for die greasing and their relative cost when combined with kerosene.

c. Explosion of the theory that oils leave black spots due to unoxidized carbonaceous matter.

d. That water cannot be used as a cutting agent.

e. The advancement of a theory that corrects the popular application of die "lubricating" to die "greasing."

f. Plastic bodies do not require so strong an oil mix.

g. Short bodies, whether containing whiting or not, require a much stronger oil mix than plastic bodies.

h. That an animal oil is not essential for the production of a good die greasing oil, either from a point of quality or cost (as mineral gelatine).

i. That an animal grease reclaimed, as in the case of de gras, is equally as good and, price the same, in our estimation there would be no preference between the two.

j. We believe we have given both the oil manufacturer and the potter some data that will enable them to get together and effect a mutual saving.

In conclusion, we wish to thank for samples and advice the O. F. Zurn Co., of Philadelphia, Pa.; the Crew-Levick Co., of Philadelphia; and the Standard Oil Co., of Newark, N. J.

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Encyclopedia Brittanica.

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DISCUSSION.

Professor Parmelee: Suppose you had a kiln full of ware which was greased with mineral oil?

Mr. Simcoe: Well, now, I know what you are going to ask, and in answer to that (*viz.*, smoked ware), would say we ourselves found that a good deal of this trouble is blamed on the oil, when it should be blamed on the fireman. We took some samples of glazed porcelain and with a torch got them as black as a hat, and they came out as clear as could be. I think that the carbonization conditions are due to the fireman, and not to the oil.

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THE TESTING OF PAPER CLAYS.

By CHARLES S. GWINN, Madison, Wisc.

The object of this paper is to describe physical tests used in determining the suitability of clays for paper-making purposes. In paper-making, a clay may be used as a filler or as a coating material, but the tests here described are intended to apply primarily to the use of clay as a filler. This is by far the more important use, since clay enters into the composition of all the ordinary printing and bond papers, as well as of many wrapping papers. The physical characteristics to be considered are: (1) presence or absence of grit; (2) color; (3) capability of disintegration; and (4) retention.

Grittiness.—Clays to be used in paper-making are desired as free from grit as possible, since the presence of such proves detrimental in many ways. The grit will be carried on the paper machine along with the stock; there it leads to increased wear on the paper machine "wires" (which are of bronze) and other machine "clothing." It also is likely to cause breaks in the unfinished sheet during the process of manufacture, and in the finished product may be the cause of specks of varying appearance. A rough way of determining the presence of grit in a clay, and one commonly used by paper-makers, is to take some of the clay and "feel" for the grit between the teeth.

The following is a more definite method for determining the amount of grit. Weigh out 200 grams of the clay under examination and add to it, in a beaker or other suitable vessel, 800 to 1000 cc. of water. Agitate with a mechanical stirrer until all the clay has been mixed with the water and well brought into suspension; this operation will probably require an hour or longer. The mixture is then screened through a 200-mesh silk bolting-cloth screen. A small quantity at a time is poured upon the screen, and a gentle stream of water is allowed to run upon it at the same time. By shaking the screen and gently rubbing the clay with the finger, the finer particles are all washed through and the grit remains behind. It can then be dried and collected for examination and weighing. By this means the amount of the grit and its character may be determined.

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The amount of grit permissible in a clay to be used for paper-making purposes depends upon the type of paper in which it is to be used as a filler. For an ordinary high-grade news-print paper, 2 per cent. would in general be objectionable, more particularly on account of the fact that news machines are run at high speed and the presence of every added amount of grit means increased wear on the machine "clothing." The character of the grit would also be of influence in deciding this point, since a micaceous grit would not be as detrimental as one of a sandy or silicious nature.

Color.—The color of a paper clay is of importance as affecting the color of the paper, even though it may be to a small degree. In determining the color of a clay it is customary to compare the clay with others which are used as standards. These standards are chosen arbitrarily and may grade from the purest possible white to a dingy gray or yellow. They may be three or more in number, and ranked, *e. g.*, as good, fair, and poor.

In conducting a test a small amount of clay under examination is mixed with water to the consistency of a paste and made into a smooth pat on a glass plate. The standard evidently nearest to it in color is similarly treated and made up into a pat immediately along side of the first. The surfaces of the two are smoothed off until they become continuous. By this means any differences in color are clearly brought out. The test pats are examined while still moist and also after they have dried out. The conclusion, however, is usually drawn from the examination made upon the dried surfaces, since it is considered that this condition is more representative of that under which the clay will exist in the paper, and that it shows, at the least, how the color of the clay may be affected by wetting and subsequent drying. By this test the color can be classed as good, fair, or poor, depending upon which of the standards it comes nearest to matching. However, it should be noted that a clay whose color might be such as to make it unsuitable for some purposes would do very well for others, *e. g.*, clays comparatively poor in color can be used in the manufacture of news print, while for the best grades of book and bond papers only the whitest

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of clay should be used. So that a clay whose color might be determined as "poor," would do very well in a hanging paper.

Disintegration.—The quality of rapidly disintegrating is to be desired in a paper clay. A simple test for this is to put a lump of the clay in a beaker of water and to note the rapidity of the disintegration. Other things being equal, a clay which fell to pieces rapidly in water would be more desirable than one which took some time to disintegrate.

Retention.—Another thing to be taken into consideration in considering a paper clay, but one which is not judged by a laboratory test, is what is known as its "retention;" *e. g.*, if of the clay furnished to a beater, 80 per cent. is found by analysis to be present in the finished paper, the clay is said to have shown 80 per cent. retention. While the retention of a clay is dependent upon particular qualities of the clay, it is also largely influenced by other factors, such as the kind of fibre used, the length of time of beating, and the amount of clay furnished. But of two clays showing under like conditions different retentions, other things being equal, the clay having the higher retention would be the most desirable. This is simply because less of it is lost in the "white water" from the paper mill.

The amount of the retention of a clay can be determined in the mill during the every-day process of manufacture. An account is kept of the amount of clay furnished to the beaters and of the amount of the paper production. Samples of the paper are taken at regular intervals, and the ash content determined, and from this the per cent. of "original" clay in the paper, taking into account the moisture in the original clay and the ash of the wood, is made known. Knowing the total paper production, the total amount of clay retained can be calculated, and from this, with the amount of clay furnished, the "retention" can be computed.

DISCUSSION.

NOTE PREPARED AFTER READING THE PAPER.

Mr. Watts: This paper is a unique addition to the literature of our Society. Few ceramists realize what a large amount of white clays is utilized for filler in the manufacture of paper and other articles not connected with the ceramic industry.

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Concerning the color of clays it is worthy of note that many clays which in the raw state have a very fine color are of a greatly inferior color when burned. On the other hand, many clays which are of a pronounced cream color in the raw state burn to a fine white color. Of the first class we have the clays of eastern Pennsylvania and Georgia, while in the second class we have the Florida kaolin and some of the Appalachian clays. As the value of a white clay for paper filler is about the same as for a clay of similar color for pottery manufacture, the value of a clay should not be estimated until it is examined both raw and burned.

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INVESTIGATIONS ON THE DIELECTRIC STRENGTH OF SOME PORCELAINS.[1]

By B. S. RADCLIFFE, Van Asselt, Wash.

In the following work on porcelains, four problems were investigated for the purposes of determining:

1. The relation between dielectric strength and thickness.

2. The effect upon dielectric strength due to varied heat treatment during burning and cooling.

3. The value of fire clays as raw materials for high tension insulators.

4. Influence of lime on dielectric strength.

INFLUENCE OF THICKNESS.

The dielectric strengths of nearly all insulating materials (porcelain included) are considered proportional to the thickness. The strengths of varnished and impregnated paper insulators are exceptions. Since no experimental data was found pertaining to the relative dielectric strength to the thickness of porcelains, it was deemed advisable to make a few simple practical tests in order to determine this point for use in the work following. For this purpose, a body having the following composition, which vitrifies at cone 12, was made: Tenn. ball clay, No. 1, 15; No. Carolina kaolin, 20; Eng. china clay, 25; spar (Brandywine Summit), 20; flint (Ohio, 8 hr. grind), 20.

The body was prepared in the usual manner according to factory practice and the trials jiggered in the form of small crocks (Fig. 1) which could be nested closely so that all pieces would receive the same heat treatment.

The trials were made in different thicknesses, varying from 1.4 mm. to 7 mm., by adjusting the jigger tool. The trials were burned to cone $12^1/_2$ and punctured under transformer oil (Fig. 2), the voltage being increased gradually by a rheostat. As soon as the trial was punctured, the current was immediately broken.

The thickness at the point of puncture was measured by a micrometer. Five to ten trials made of the same thickness were punctured in each case. Whenever puncture took place

[1] An abstract of work done in 1909–10 in partial fulfilment of requirements for M. S. degree in Ceramics at the University of Illinois, under supervision of R. T. Stull.

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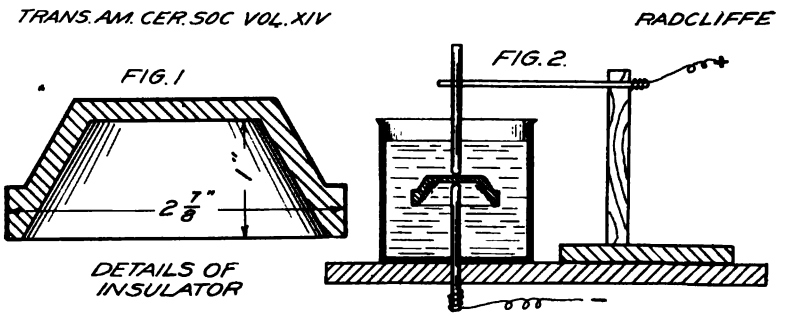
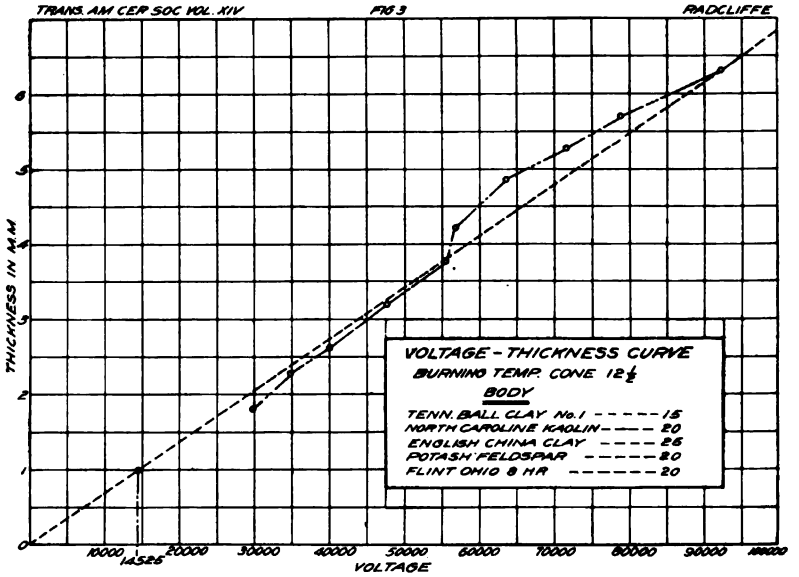


through a flaw, the trial was rejected. The voltages required for puncturing sound trials of the same thickness were averaged, the thickness being plotted on the ordinate and voltage on the abscissa (Fig. 3).



Calculating the average puncture voltage per mm. thickness for all trials tested, assuming that the puncture voltage is directly proportional to the thickness, gives a voltage of 14,525. This point is plotted and the heavy dotted straight line passes

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from the origin through it. Owing to the fact that a voltage higher than 100,000 was not available, pieces over $6^1/_2$ mm. in thickness could not be tested. However, the limits covered exceeded the requirements in the future tests.

Some interesting results were obtained by puncturing the same test piece repeatedly in the same spot. One piece, 5.7 mm. in thickness required 83,800 volts, and was given a second test and punctured at 79,000 volts, a third test required 59,300, a fourth 51,200. When the trial was shifted to a new place, the voltage required to puncture it was 77,500. Other trials were treated in the same manner giving similar results. Repeated tests through the same line of puncture weakened the dielectric strength at that point, but not until several punctures did the porcelain become too weak to resist a fairly high voltage.

Apparently the current fuses the porcelain in passing. Upon breaking several pieces through the line of puncture a glassy appearance was always noticeable.

INFLUENCE OF VARIABLE HEAT TREATMENT.

There seems to be no data available pertaining to the effect of rate of burning and cooling upon the dielectric strength of porcelains. In order to throw some light upon this subject, four porcelain bodies were selected from the work of Bleininger and Stull on "The Vitrification Range and Dielectric Strength of Some Porcelains." These bodies are here designated by A, B, C and D. Besides these, E was made by blending the four.

Body	Georgia kaolin	Tenn. ball No. 1	N. Car kaolin	Eng. China clay No. 7	Potash feldspar	Ohio flint
A.....	50	..	..	..	40	10
B.....	..	55	..	..	15	30
C.....	..	..	55	..	25	20
D.....	..	..	..	60	20	20
E.....	5	9	27	18	23	18

Five more bodies were made similar to these except that soda feldspar replaced the potash feldspar by theoretical molecules. These bodies are designated as A1, B1, C1, D1, and E1.

Twenty trials were made from each of the ten bodies. These

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trials were divided into four sets, each set containing five trials made from each body. Each set was burned and cooled under different conditions. Set 1 was burned to cone 10 in six hours and cooled slowly in order to determine the effect of quick firing and slow cooling. Set 2 was burned to cone 13 in six hours after which air was passed through the kiln cooling the temperature down to cone 02 in one hour. The kiln was then allowed to cool slowly. Set 3 was burned to cone 10 in six hours then the temperature was gradually raised to cone 12 in an additional 14 hours, then carried rapidly to cone 17 and held for 2 hours. The kiln was then allowed to cool slowly. Set 4 was burned to cone 10 in 6 hours, gradually raised to cone 13 in an additional 18 hours and held for 20 hours. The kiln was then cooled down to cone 2 in five hours, then allowed to cool slowly.

C and C1 in the first burn showed 2 per cent. porosity but all the other bodies were well vitrified.

AVERAGE VOLTAGE PER MM. REQUIRED TO PUNCTURE TRIALS.

Body	Part 1, Cone 10	Part 2, Cone 13	Part 3, Cone 17	Part 4, Cone 13
A	13260	13120	12600	13070
A1	12840	13100	14300	13870
B	13400	13000	13500	13000
B1	14000	13640	13620	14160
C	10320	13960	12760	13180
C1	9180	13220	13820	13860
D	14540	13150	13680	14100
D_1	13400	13920	13100	13520
E	13550	13470	14660	12850
E1	13560	14820	14100	13860

The tests show that there is not a very wide difference in the dielectric strengths of the different bodies or in the manner of heat treatment. By taking the average puncture voltage per mm. for each different body for the four different burns (excluding C and C1 which were porous in the first burn), we have the following table which shows that the soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies in all cases except in bodies D and D1 in which case D shows a higher dielectric strength than D1.

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Potash spar bodies	Average voltage per mm.	Average voltage per mm.	Soda spar bodies
A	13012	13527	A–1
B	13225	13855	B–1
C	13300	13633	C–1
D	13867	13485	D–1
E	13632	14185	E–1

In order to get a comparison of the effects of variation in heat treatment, the average voltage per mm. is taken of the ten bodies for each of the four different burns. In averaging the first burn, bodies C and C1 are rejected on account of their porosities. The percentage variation between maximum and minimum puncutre voltages is less than 0.55 per cent. showing that the dielectric strength was substantially unaffected by the variations in burning and cooling from cone 10 to cone 17.

Burn	Cone	Average puncture voltage per mm.
Part I.....	10	13569
Part II.....	13	13540
Part III.....	17	13614
Part IV.....	13	13547

FIRE CLAYS AS RAW MATERIALS FOR HIGH TENSION INSULATORS.

The trade demands a white porcelain body for high tension insulators. Frequently a dark colored glaze (usually brown) is called for. If a colored body could be employed containing a high per cent. of fire clay, a cheaper body and a more uniform color of glaze would be the result. Insulators made from No. 2 fire clay or stoneware clay do not show a high dielectric strength. These clays vitrify at or near cone 8 while the white high tension porcelain insulators vitrify around cone 12.

In order to obtain bodies which would vitrify near cone 12, three fire clays were blended triaxially (Fig. 4). The three fire clays selected were: Olive Hill flint fire clay (calcined); Olive Hill No. 1 plastic fire clay; Bloomingdale[2] No. 2 plastic fire clay.

[2] An excellent stoneware clay, vitrifying at cone 8.

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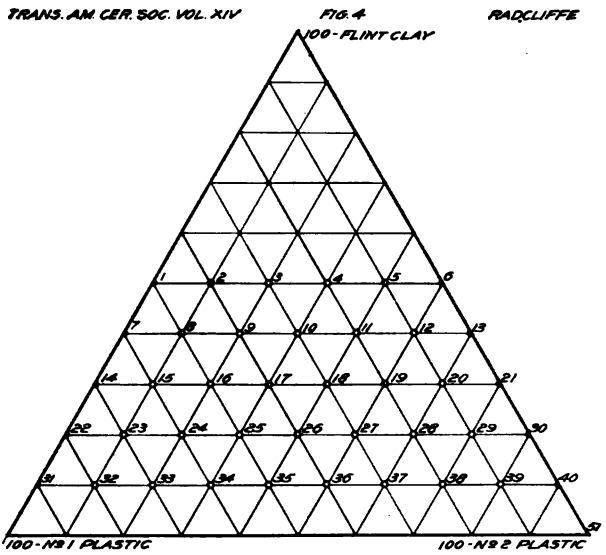

Five trials of each body were made and burned to cone $12^1/_2$. The porosities and puncture voltages were determined and averaged. These results are plotted on the triaxial diagram (Fig. 5), the dotted lines representing porosities and the heavy solid lines puncture voltages per millimeter thickness.

The results show that 90 parts No. 1 plastic fire clay and 10 parts calcined flint fire clay give a body of the highest dielectric strength at cone $12^1/_2$, and even though this body had 1 per cent. porosity, it compares very favorably with the best white porcelains in strength, 14,000 volts per mm. being required to puncture it.

When No. 2 fire clay or stoneware clay replaces the No. 1 plastic clay, the flint clay remaining constant, the dielectric strength is lowered even though the porosity is lowered at the same time.

Bodies containing 50 per cent. or more of No. 2 clay showed evidences of a "bleb" structure, which weakened them, causing them to puncture at a low voltage. The substitution of 10 per cent. No. 2 clay for No. 1 in body 31, which gives body No. 32,

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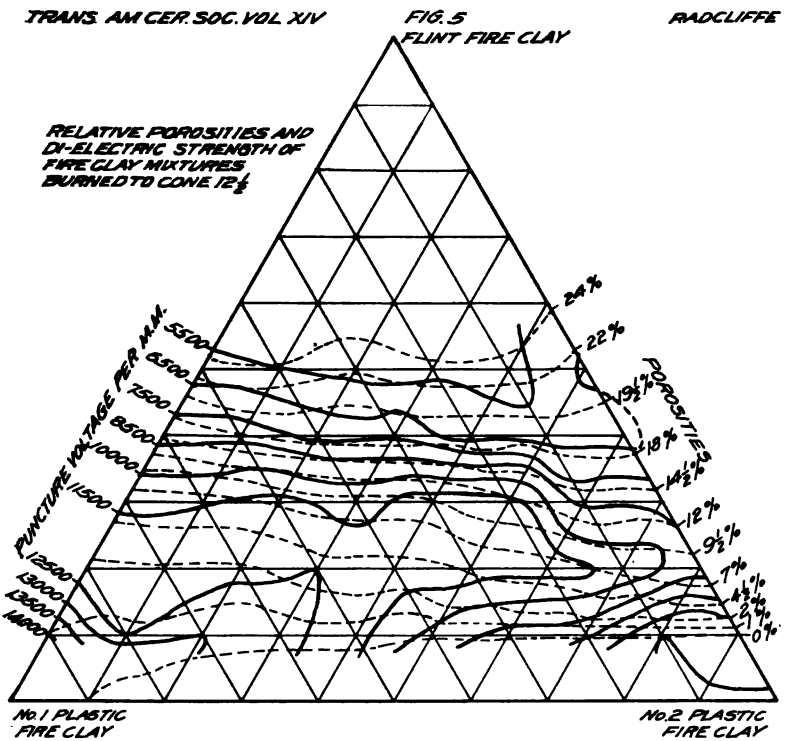

did not materially lower the porosity, yet it lowered the puncture voltage from 14,000 to 12,500.

Trials which were subsequently made from bodies 14, 22 and 31 and burned to cone 14 gave a porosity for 14 of 1.34 and a puncture voltage of 13,600 per mm. The porosity of No. 22 was 0.08 and its puncture voltage 14,100 per mm. Porosity of No. 31 was zero and its puncture voltage 14,600, an increase in voltage of 600 for a decrease in porosity of 1 per cent. The white porcelain body of highest dielectric strength found in the foregoing work is the soda feldspar body E1, giving a puncture voltage of 14,820 per mm. in the part II burn. The potash feldspar body of highest dielectric strength is D, showing a puncture voltage of 14,660 in the part III burn.

In so far as dielectric strength is concerned, the foregoing

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evidence indicates that vitrified bodies made from refractory fire clays stand on an equal footing with white porcelains for high tension insulators.

Good colored high tension insulators can be made from a body composed of No. 1 plastic fire clay (part of which may be calcined) and a small amount of feldspar to assist vitrification. The use of flint fire clay in the body lowers the dielectric strength by increasing porosity through its refractoriness. The plasticity, working properties and shrinkage of a fire clay body can be controlled much better than white bodies and at the same time, it would be cheaper in composition.

INFLUENCE OF LIME ON DIELECTRIC STRENGTH.

In order to determine the effect of lime upon the dielectric strength of porcelain, the following bodies were made in which $CaCO_3$ was used to vitrify the bodies in place of feldspar. Part of the clay was calcined in order to control working properties. The trials were burned to cone 14 and porosities and puncture voltages determined. These results are given in the following table.

Body	Tenn. ball C. No. 1	N. Car. kaolin	Ohio flint	Calcined N. Car. kaolin	$CaCO_3$
F	10	45	22	23	0
F1	10	45	22	22	1
F2	10	45	22	21	2
F3	10	45	22	20	3
F4	10	45	22	19	4
F5	10	45	22	18	5
F6	10	45	22	17	6
F7	10	45	22	16	7
F8	10	45	22	15	8

The results show that 6 per cent. $CaCO_3$ has produced a non-porous body at this temperature which does not show a high dielectric strength, and that each increase in CaO has increased the dielectric strength. F5 containing 5 per cent. $CaCO_3$ has a porosity of 12.84 per cent. F6 shows that an increase of 1 per cent. of $CaCO_3$ has lowered the porosity to almost zero.

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Body	Per cent. porosity	Average voltage per mm.	Body	Per cent. porosity	Average voltage per mm.
F.....	28.02	..	F4.....	12.65	..
F1.....	27.60	..	F5.....	12.84	5000
F2.....	20.52	..	F6.....	0.05	6000
F3.....	17.81	..	F7.....	0.03	6700
			F8.....	0.06	8000

When the puncture tests of F6, F7 and F8 are compared to those of feldspar porcelains of the same porosities and burned at the same temperature or even a little lower, it is observed that the dielectric strengths of the feldspar porcelains are from one and one-half to twice those of the lime porcelains.

CONCLUSIONS.

Conclusions which may be drawn from the foregoing work indicate that:

1. For all practical purposes, the dielectric strength is proportional to the thickness of the porcelain, which is in confirmation of that assumption.

2. Rapid burning or slow burning, rapid cooling or slow cooling do not materially affect the dielectric strength of high tension insulators so long as such treatment does not develop blebs, cracks or other flaws.

3. The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increased the dielectric strength.

4. High-grade fire clays are capable of making high tension insulators giving as high a dielectric strength as the average potash feldspar porcelain vitrifying at the same temperature.

5. The substitution of a stoneware clay for No. 1 plastic fire clay lowers both the maturing temperature and the dielectric strength.

6. A body made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength.

DISCUSSION.

Mr. Purdy: I note that he has a series in which calcium carbonate is varied against calcined clay. An explanation of the

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philosophy of a substitution of such unlike materials would be of interest.

I note also that he reports that a piece which has already been punctured will show a lower but relatively high strength when tested the second time at the same point and the same high strength when the same test piece is punctured at a new point. The only fact of value in these observations is the efficiency of oil as a non-conductor. When puncturing under oil the hole thus caused is filled with oil and not by glass as Mr. Radcliffe thinks. You can not re-test a punctured piece in the air as they did in the oil. In fact they could not have tested those shallow pieces in the air at all because of arcing around. Their data, therefore, on these two points is of value only for insulation under oil. Their conclusion should have been that their porcelain test pieces had but little, if any, better dielectric strength than did the oil they were using.

Prof. Stull: In order to satisfy Prof. Purdy's interest regarding the replacement of calcined clay by calcium carbonate, I will say that the calcined clay was employed merely for controlling the working properties and drying shrinkages of the bodies, as was mentioned when the paper was read. No attempt whatever was made to get a comparison of the bodies by variable lime-calcined clay. The object in view was merely to obtain vitreous bodies by using lime without resorting to additions of feldspar, and to compare the dielectric strengths of these lime bodies with those of feldspar bodies previously made.

There is no "hole" left after the porcelain has been punctured. Several of these crock shaped test pieces, after puncturing, were used as convenient receptacles for calcining small samples of kaolin at 1000° C. At this temperature the oil was completely burned off. Some of these trial pieces were broken through the line of puncture after they had served their purpose in calcining clay and these pieces showed plainly that the "hole" was filled with a glass.

Mr. Radcliffe shows that repeated puncturing through the same spot gradually weakens the dielectric strength. If puncturing leaves a hole and this hole is filled with oil, then why would

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not repeated puncturing after the first give the same voltage readings for puncturing the column of oil filling the hole?

The use of the oil bath is merely to prevent arcing. If the trial pieces had been made of suitable size and shape to prevent arcing when tested in air, there is no reason why they would not have shown the same dielectric strengths in air as they did in oil.

The results are comparative whether the porcelains are tested in air or in oil. Either set of conditions would show the porcelains of highest dielectric strength.

NOTES PREPARED AFTER READING THE PAPER.

Mr. Minneman: This paper by Mr. Radcliffe is a valuable addition to our ceramic literature, for the reason that so little experimental data is available along these lines.

I think, however, that certain of his conclusions are drawn too directly from his actual results, neglecting other conditions which are bound to enter in.

In regard to the dielectric strength of soda-feldspar *versus* potash feldspar, Mr. Radcliffe says: "The soda feldspar bodies have higher dielectric strengths than the corresponding potash feldspar bodies" and "The average of all tests made in this work showed that the molecular substitution of soda feldspar for potash feldspar in a porcelain decidedly increases the dielectric strength." However, upon looking over the individual test results, it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show the higher dielectric strength. Averaging the dielectric strengths of all the soda feldspar bodies and all the potash feldspar bodies, we find the soda feldspar bodies have only about 2.5 per cent. higher dielectric strength than the corresponding potash feldspar bodies. This appears to be a decided increase in the dielectric strength, but when it is remembered that, in the method used in testing, voltage readings accurate to several per cent. are almost impossible, and variations up to 10 per cent. are quite possible, this difference of 2.5 per cent. seems almost negligible.

The voltage readings in these tests were taken, I understand, from a voltmeter placed across the low tension side of the

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transformer, getting a calibration curve between the volts primary and volts secondary by means of a needle gap in the high tension side. The readings could, therefore, not be more accurate than readings from the needle gap which would be from one to four per cent., depending upon the experience of the observer. Add to this numerous uncontrollable variables, such as varying weather conditions, growth of charge in the circuit, variation in wave form and the time element in testing and it is evident that a wide divergence is quite possible.

That such a variation occurs, may be seen from the results obtained by Messrs. Bleininger and Stull, Vol. XII, Trans. A. C. S., p. 638, who made tests on the same porcelains fired at approximately the same heat treatment and tested with the same, or a very similar, apparatus. Comparing their results on the same trials and with Radcliffe's results we find variations up to 25 per cent.

Considering these points, I should say that Mr. Radcliffe's results tend to show that the dielectric strength of a porcelain is the same whether made from soda feldspar or potash feldspar so long as the porcelain is well vitrified and dense.

In regard to the use of lime, Mr. Radcliffe concludes that "a porcelain made vitreous by the use of lime without feldspar gives a porcelain of low dielectric strength."

It must be remembered that Mr. Radcliffe replaced his feldspar with lime and calcined china clay, thereby making a body of an entirely different structure. It is evident that a body made up with calcined clay and lime in place of feldspar would behave quite differently, due to the lesser distribution of the lime particles and the resulting differences in fusion, just as a body made up with equivalent amounts of sodium carbonate and calcined clay would differ from a body made up with soda feldspar. Had the clay and lime been fritted and ground until a homogeneous mixture was reached before being used in the porcelain, I think that entirely different results might have been obtained. I agree with Bleininger and Stull that dielectric strength "depends more upon sound vitrification and good mechanical structure than upon chemical composition."

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Mr. Radcliffe's results do, however, show that lime used in porcelain in this way materially shortens the firing range.

The great volume of high voltage porcelain is not used under oil but in air and tests under oil often give entirely different results than do air tests. It is particularly noticeable that a porcelain not completely vitrified and having considerable absorption shows up very well when tested under oil, but breaks down much earlier when tested in air with the bottom of the test piece placed in water as is done in commercial tests.

Mr. Radcliffe mentions the puncturing of a piece under oil repeatedly in the same spot. When testing porcelain in air, after puncture once takes place there is a continuous flow of the current, and the piece ceases to act as an insulator. When testing under oil, however, this repeated puncture at a lower voltage often takes place, which leads me to believe that the oil protects the punctured spot sufficiently to give considerable insulation after the first puncture.

Consequently I should say that tests made in air, more nearly approximating conditions under which high voltage porcelain is used commercially, would be of much more practical value.

Prof. Stull: The question of experimental errors enters into all research work of this character. In theory, however, there is such a thing as absolute accuracy. The value of research work depends largely upon the accuracy in executing the work and the extent to which experimental errors are avoided or eliminated.

One of the greatest sources of error which Mr. Minneman failed to mention is due to variations in structure of different pieces made from the same body. It is impossible to eliminate minute air bubbles and to mould two pieces of porcelain so that they will have identically the same structure.

Where it is impossible to eliminate experimental errors or to deduct such errors by calculations from known data, it is customary to make several tests and to consider the mean average as a means of reducing such errors to a minimum.

As has been mentioned, Mr. Radcliffe made from five to ten different puncture tests for each different body under each different set of conditions, excluding all trials in which flaws due to

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moulding were apparent and taking the mean average of apparently sound pieces.

Mr. Minneman states that "it is seen that in eleven cases the corresponding soda feldspar bodies show higher dielectric strength while in the remaining eight cases the corresponding potash feldspar bodies show higher dielectric strength."

It was stated in Mr. Radcliffe's paper when read that "bodies C and C1 are rejected on account of their porosities" (in the first burn). Since these two bodies are porous they are not at all comparable with the others which were well vitrified, hence, it is legitimate and proper to exclude them from the calculations. Excluding C and C1 in the first burn, it is observed that the comparison is as twelve to seven, as Mr. Minneman has evidently made an error in count.

Since five trials of each porcelain for each of the four burns were tested, the average puncture voltage per mm. (excluding C and C1 in the first burn) is calculated on ninety-five trials punctured for each type of porcelain. Taking the average of such a large number of tests tends to give an accurate comparison.

The physical properties of ceramic mixtures depend upon composition and method of treatment. The treatment of the potash feldspar porcelains and the corresponding soda feldspar ones were carried out as nearly alike as possible. Since the two different kinds of feldspars are bound to exert some differences upon the physical properties, and one of these physical properties is "dielectric strength," it is more logical to conclude that the substitution of soda feldspar for potash feldspar has increased the dielectric strength since this conclusion is backed by the average results of ninety-five puncture tests of each of the two types of porcelain.

Mr. T. H. Armine: The puncture tests made upon the porcelains referred to in Mr. Radcliffe's paper were made under my supervision in the Engineering Experiment Station at the University of Illinois.

The accompanying sketch shows the connections used in

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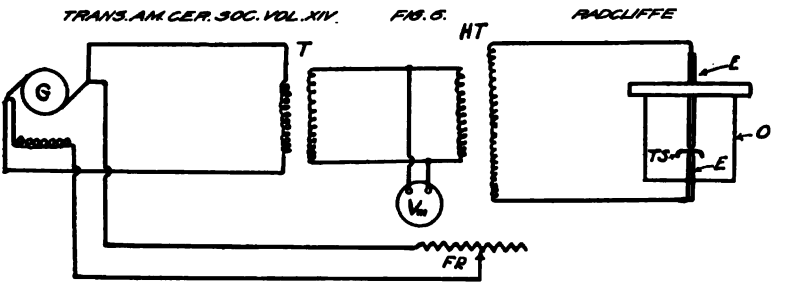

the test: G is a generator of 60 kilowatts capacity which produces practically a sine wave of electromotive force. T is a transformer stepping the voltage of the generator up by a four to one ratio. HT is a transformer of 10 kilowatts capacity which is designed to step from 440 up to 100,000 volts. FR is the field rheostat of the generator by means of which the high tension voltage was varied. O is a stoneware jar having a brass electrode, E, inserted through a hole in its bottom. A similar electrode, E^1, was arranged in such a manner that it was brought in the same straight line as E and so that it could be pulled up away from E to permit of putting the porcelain sample TS between the electrodes.

The first procedure was to obtain a calibration curve of the apparatus. The connection was removed from the electrode E and E^1 and a needle gap was placed across the high tension side of the transformer. With various settings of the needle gap the voltage was gradually brought up by varying FR until the discharge took place across the gap, at which time the voltage on the low tension side of the transformer was read by means of the voltmeter Vm. In this way the relation between "volts primary" and "length of the needle gap" was obtained. Then by means of the well known A. I. E. E. curve between "distance between needle points in air" and "volts," the "centimeters width of needle gap" were translated into "volts secondary." This calibration was repeated several times and good checks were obtained so the average curve between "volts primary" and "volts secondary" was adopted as the calibration curve.

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In making the puncture tests the connection was made as shown in the diagram, a porcelain test piece, TS, was placed between the electrodes and the stoneware jar O filled with transformer oil. The voltage was gradually brought up by varying FR until puncture took place, at which time the "volts primary" were read by means of the voltmeter Vm. By means of the calibration the curve "volt secondary," that is, the volts to produce rupture, could be obtained. In all the tests care was taken that the rate of increase in voltage was uniform for all samples.

In Mr. Minneman's discussion of this paper the question of accuracy of the results obtained is brought up. Since the calibration curve was obtained by reference to a needle gap it may be in error by as much as 4 per cent. Since it was made all in one day under as constant conditions of weather, etc., as possible and since several checks were made it is probable that the error in calibration is less than this. However great the error in the calibration curve is, it is a constant error and affects the reading only when considered as absolute values of voltage and does not affect the relative values obtained for the various samples. For instance, the tests upon soda feldspar *vs.* potash feldspar involve none of "the uncontrollable variables such as varying weather conditions, growth of charge, variation of wave form and time element," mentioned by Mr. Minneman. The values obtained for these two porcelains should be closely comparable even if the absolute values of voltage were seriously in error since the errors should be the same for both sets of tests.

Mr. Minneman also mentions that "when testing a porcelain in air, after puncture takes place there is a continuous flow of current and the piece ceases to act as an insulator." This same action takes place with tests under oil. At the instant of rupture the current follows the arc and continues to follow it as long as the voltage is on in the same way as it does with a test in air. A second application of voltage in the same spot does show that there is still considerable dielectric strength after the first puncture. This dielectric strength is not, however, due to the protective effect of the oil. The current which follows the arc fuses the porcelain and when the circuit is broken the fused porce-

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lain solidifies in place, forming a glassy spot. Due, perhaps, to flaws and to the presence of foreign material such as carbonized oil, which probably prevents the formation of a homogeneous structure, the strength on second puncture is less than on the first. The voltage at which a sample will puncture the second time has, I believe, no relation to the real dielectric strength, *i. e.*, on first puncture, of the porcelain sample. I believe that the only serious effect of testing under oil would be with very poorly vitrified porcelains such as are obviously not fit for high tension insulators. In testing these porous porcelains comparable results possibly would not be obtained under oil.

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THE ESTABLISHMENT OF TECHNICAL TRAINING SCHOOLS FOR ARTIST-CRAFTSMEN IN CONNECTION WITH INDUSTRIAL PLANTS.

By M. E. Cooke, Columbus, O.

Progress in the Art Industries, as in civilization, is measured by the use man makes of his higher, or reflective and creative, powers; and trained industrial skill is a powerful factor in commercial progress as well as individual.

Speaking of the marvelous expansions of German industries, a recent London journal comments thus: "It is, of course, impossible to locate with certainty the actual effects of any given cause, but there can be little doubt that the growth of the many immense industries is traceable to the system of education that has directed all the available powers of scientific knowledge and research upon industrial art problems."

In the past six years in England, five technological universities have been established to meet industrial needs, and stress laid upon the branches of science most useful in industrial art.

Until the past few years, this field of educational development has been neglected in America. But today the education whose motive is to prepare workers for productive efficiency is the education the modern world recognizes as a necessity, and it is trying to meet this need by establishing vocational and trade schools. These are, of necessity, elementary, though giving the boy or girl a start in the right direction.

But where can the clay workers find the training that will enable them to be economically efficient in bringing to America clay products of ultimate beauty of form and color? In the art schools he learns only abstract art; instruction is cultural with few or no facilities for the study and practical application of his knowledge. One of our strongest and most American sculptors has declared, "Our art schools, as now conducted, are retarding progress," and that if we want to find American artists, we should turn to the men who are concentrating into great masses our industries, who are dividing the continents, letting the sea into the land, and the products out. These are the men of dreams, of imagination. Our artists, must speak with the same voice; it must be the concrete doing, not abstract, if they

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put the soul of all this power of natural resource and mechanical efficiency into our sculpture and architecture. How else shall we utilize to the fullest extent the wonderful beauty that science and practical training have made available in the clay industries?

And where shall the American boy and girl find their training to put honestly and sincerely the story of American life and aspiration into the most beautiful medium nature affords, unless they know it from every standpoint? You will, I feel sure, agree with me that clay holds for the unwary mortal who ever touches it a subtle lasting charm, from which he never escapes, beginning, perhaps, at the mud-pie stage, lasting through struggling days of investigation and experiment, responsive to his will as is no other medium of expression, and always at every stage its own compensation.

Given the opportunity, the clay modeler or designer will be more faithful to his chosen vocation, I doubt not, than the worker in any other craft. Where could he find a more comprehensive and inspiring knowledge of clay than in one of our great industrial clay plants, where practical experience, mechanical skill, and science combine to produce the technically perfect clay product?

In production of pottery, tiles, and special architectural sculpture, the clay product has, to a large degree, reached perfection —from the artistic standpoint. But these are still undeveloped fields for the artist-modeler, if the clay products keep pace with the demands of the architects for distinctive design and greater simplicity in utilizing the technical beauties of clay for architectural purposes at moderate cost.

The technical schools, where art is allied, are doing much for pottery and tiles; but in the larger field of architectural sculpture, the American craftsman has an almost undiscovered country in which to create the distinctive work that lifts the brick or terra cotta structure out of the commonplace. We hear much of "American Art," but will we have any real American art until we begin—as all races have begun, at the structural foundation, with clay as our medium and with skilled craftsmen, having some intelligent knowledge of their material,

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its possibilities as well as its limitation—to set free the spirit of beauty that lies latent in every lump of clay?

In the ancient crafts, the system of apprenticeship directed and organized the vocational work, and doubtless this system, as inherited by certain of the great vocations of the middle ages, was the most perfect system of vocational education that the world has ever known. Was not the secret of success in the apprentice schools due to the fact that the workers were put at once to the concrete doing of things of practical use and purpose?

Extension work in some mechanical engineering colleges gives the men practice work in the industrial plants. Last year, the American Institute of Architects appointed a committee on education, and their recent report, made after systematic study of education applying to architecture, is encouraging. Columbia College, acting upon suggestions of the committee, established definite courses for extra-collegiate students, given under university auspices, that have been surprisingly successful. They are called extension courses, and cover all first and second year work. The University of Pennsylvania is giving a similar course.

In Boston, the Institute of Architects, with some aid from the Society of Architects, has taken all responsibility for extension work there, where the instructors are the pick of the Harvard and Technology faculties.

Can not some practical and effective means of education be formulated for the clay workers, through coördinating the work of the technical departments of our universities with practical training in the great industrial plants, under careful instruction of artists and sculptors?

Is the development of the art side of our clay products going to keep step with the technical and practical sides in the clay industries, unless we have skilled workers, knowing intimately and intelligently the body, soul and spirit of clay? In the wonderful progress of developing the clay industries along certain lines, have we not left Art imprisoned in the blunger?

To reach the higher standard of artistic excellence demanded by the public, through the architects, a broader, more effective,

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and thorough coördination of practice, science, and art must be accomplished through practical education.

In his report to the U. S. Bureau of Education, Bulletin 6, upon the apprenticeship system in relation to industrial education, Carroll D. Wright says: "A combination of apprenticeship and academic education is what we need. With modern development of industry there is overwhelming evidence all over the country that demand for skilled labor is not met by the supply. It is generally conceded by best educators that the industrial school does not, and cannot turn out full-fledged skilled mechanics and artisans ready to take up their trade."

In recent years in America, each industry that has some form of apprenticeship has developed its own type of school, though general systems are much alike.

The General Electric Company, Lynn, Mass., teaches theory first, then practice. The New York Central Lines have what they call "a rational apprentice system," reversing that of the General Electric Company, giving practice work in shops first. These schools are established at eight or nine points on their system, and provide: first, apprentice instructors to give close supervision and instruction in the shop; second, a school conducted by the company during working hours, the apprentices paid for attendance, where mechanical drawing is taught in a practical way. A course of problems suited to their work is given the apprentices to work out in practice. The boys, under this system, take great interest in their work, and because of the principles learned in connection with their educational studies, are better able to carry out instructions given them, and their earning power is increased.

The Ludlow Manufacturing Company, of Massachusetts maintains a school giving instruction of two kinds, the practical part in the mill, the theoretical in the school, the whole course embracing about four years. A special shop arithmetic, covering all the operations and calculations needed in the mills, was prepared by the overseers and director of the mills. Designing and all natural sciences relating to textile manufacture are studied, also history of textiles. Manual training is given in constructing rooms. In connection with their study of physics,

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they examine and grade fibres, testing them for strength, moisture, etc.

This is Industrial Art education of a high order.

Is it not sensible and along progressive lines to regard the art student choosing clay as a medium as so much raw material plus unknown creative power, originality of conception in design and color, and requiring a scientific development to secure economic efficiency just as the brother clay we study so profoundly to mould into bricks and terra cotta.

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Prof. Bleininger: In Europe the porcelain manufactories under government control, such as the Royal factories at Berlin, Dresden, Nymphenburg, etc., serve to some extent as training schools for artists though, of course, their leading function is to develop artistic progress along new and original lines. Many German artists now engaged in factory studios owe their training to the above institutions and in the study of European pottery this influence must not be underestimated.

Mr. Cowan: The problem of technical ceramic education is one in which I am naturally very much interested. As some of the members of this society know, I have charge of the work along this line in the public schools of Cleveland. In this discussion I desire to give a frank statement of the work we are doing, conditions as I find them, and some ideas of my own about the needs of such education.

Cleveland has taken a prominent position in the recent development of technical education, if not the most prominent part, under the leadership of Mr. Wm. H. Elson, a man big in every way and well able to carry out his progressive ideas.

Under Mr. Elson's administration has grown up a broad system of technical and vocational training in the public schools as represented by two technical high schools, each the result of an outlay of three-quarters of a million dollars, two high schools of commerce, manual training and applied art buildings for each of the seven academic high schools, as well as an industrial school and manual training and domestic science centers where all the children in each of the eighty some grade schools have

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a little practical training. This is but a beginning, although a better one than any other city, of which I know, in this country has made.

As Mr. Elson was much interested in pottery and thought its study could be introduced into the school system with value, a department was well fitted out in the first of the technical highs to be built, four years ago. The second of the technical highs was built this past year, and I am now completing a pottery equipment for this school.

The pottery work was made a part of the regular art course in the technical and academic high schools by taking it as the first of the crafts, as the first method of making practical their study of form and applied ornament. This application we believe the best way in which young children can work out the theories of form and ornament which are given them, and, more than this, in time is bound to exercise a desirable effect on the demand for good things in ceramics, because when grown these children will always have an eye for things made of clay, and an appreciation much keener than the appreciation of those whose interest is not so intimate. Of this use of pottery work there has been but little criticism and much commendation.

So, even though only for selfish reasons, I believe it would be worth while for the members of this society to encourage this elementary pottery work in the public schools of the country instead of criticizing it as I have heard done because of its crudeness. However poor it may be, it is usually the children's best effort and the more apt he or she will be throughout their life to truly appreciate pottery or other ceramic work on which considerable skill has been expended.

I have said there can be but little criticism of this elementary work as a part of the art course. It being out of the question for all of the students after making and decorating their pottery to spend time to mix glazes and learn to fire, it becomes necessary that some one of sufficient skill and experience do this glazing and firing. Being the only one with these qualifications, I have had this to do. The criticism, as voiced by several, is that the glazing and firing is the part of the work which is really important, that the shaping of the piece and its ornamentation

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is merely incidental, and consequently the child acquires an exaggerated idea of the importance of its own part in the production of the piece, since it takes no further part in the work.

There is much justice in this criticism, but the advantages of the work, as I see it, far outweigh its disadvantages. I will not take space to argue the question but must say that the general ceramic product of the country looks as though many of the manufacturers thought the form and decoration of the ware to be of little importance.

In addition to the elementary pottery work common to all the art departments, it was planned to gradually develop such interest in the pottery work that eventually more advanced classes could be organized in the technical highs where the specially interested pupils could further develop whatever talents they might possess.

The Board of Education, however, has a rule to the effect that all classes must consist of at least twenty members, and this was rather fatal to the success of this plan, too few selecting the work in the day classes. Interest in the night classes, however, is quite general and success here seems assured. The pupils in the night classes are of mature age; and by the interest shown, it will not be long before Cleveland will have a number of producers of amateur art pottery, eventually making this city, we hope, one of the centers for the making of such ware.

This country may not have as many college graduates in ceramic work as can be used, but what the country really *needs* is a trained body of workmen, and the reason why is largely to be found in the peculiar state the clay industries are now in. Throughout the whole series of ceramic products from the coarsest to the finest, there is a condition of affairs common to no other industry with which I am acquainted. This condition is a lack of concentration of production. In the steel industry we have concentration; we have immense plants with thousands of workmen, and so of necessity hundreds of positions of trust, requiring educated men to fill them. In such an industrial condition extensive research laboratories are possible. Even though a smaller plant could make every bit as good use of knowledge so gained through research, it can hardly afford the expense attached to it.

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This lack of concentration in all the branches of ceramic work is, to any one who has compared it with other industries, quite evident. In the case of the coarser wares, such as brick, where the cost of transportation makes that ware of necessity a local product and of local consumption, it is the limitation of this consumption that limits the size of the plant. In whiteware manufacture we have much the same condition but without the same governing cause, for the product is not usually of local consumption. We have, however, a large number of small plants, often grouped together in rather large numbers but for the most part independently managed.

If we take one of these small plants and analyze it we find it is manned by, we will say, several hundred workmen, two or three foremen, and one superintendent. There is usually a business manager or general manager, and thus we have the full complement of men. The only position open in such a plant to a college graduate is that of foreman or superintendent, neither of which are very alluring as compared to positions in other industries. Neither could a college graduate fill these positions without several years work at the bench. To say that every pottery needs a chemist is all right in theory but to my mind there is a more pressing need.

The conditions I have been citing of the whiteware industry are just as true of the other industries, brick, tile and terra cotta. Though there are some large plants in each of the branches of clay work, the largest is insignificant compared to some other industries.

The foremen and superintendents of these small plants are drawn of course from the ranks of the workmen. The workmen are of slight education, very few have anything better than a grade school education and many not even that. The slight school training they have had is the first lap of a course of education which has been developed with an eye single to a higher education and not fitness for life work. So outside of the fact that they have learned to read, write and figure a little, provided they can make practical the usually impractical school mathematics they have been taught, they have merely grown up and gone to work.

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Now, it has been proven by actual figures in Cleveland as elsewhere that if the high school course is made of practical benefit to these children a much larger proportion will stay in school, and go out to earn a living much better fitted for progress, than would otherwise be the case. Indeed, where the high school can be made of direct and practical benefit, it is proven that many will go to high school and graduate who on the other hand would never have gone at all. Surely no one will have the hardihood to question the value of education which will do this.

Cleveland has a multitude of industries, and such practical training as it has been possible to give these students has as yet been along the lines of general, mechanical, and artistic work, while the problem of direct training along special lines has only begun.

On the other hand, what a wonderful opportunity there is in the whiteware industry to give to children in the pottery centers a chance for this special education, a chance for a broader understanding of their life work. We have cities such as East Liverpool, Ohio, where the potteries make up the bulk of the industrial work of the cities. In these places we have thousands of children growing up with no real help from the city schools in the work which a majority of them must take up. Special courses should be arranged in the *high school* where chemistry applied to ceramics and art work applied to form and decoration of claywares could be taught and equipment furnished to enable pupils to get at least a slight knowledge of the different operations of manufacture and possibly some skill in certain operations. These schools should be made continuation and night schools as well, to get the maximum of good from them.

The continuation school as it is generally considered works out on some such plan as this. Each state has child labor laws which are more or less strictly enforced. A limit is set at, we will say, fourteen years of age, below which no child is allowed to go to work. A higher limit is set below which a child can go to work with permission of the proper authorities. During this interval of work with permission, the continuation school is most beneficial, in as much as this permission can be granted with the understanding that the equivalent of one half day a week

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will be granted the child to attend school. In addition to this, the school is open to all above this minimum working age for as long as can be arranged with the employer. Also night classes are established where the schooling can be continued as long as the pupil thinks best. It should not be hard to understand the great good that would come of such opportunity offered to those ambitious to get along in the field of clay work. England and Germany are working along these lines, and have been for some time. It is about time Americans woke up and lived up to their supposed reputation of being progressive.

America is getting too far behind the other countries in the production of fine ceramics. Our colleges where ceramics are taught have had a lasting and remarkably good effect on the value of ceramics from the engineering and scientific standpoint. The graduates and instructors of these schools have solved many pressing problems the manufacturers have had to meet. But the pressing need of this day is a better and more intelligent class or workmen. A class of men with a training such that it will be possible to draw from them a better and more intelligent class of foremen and superintendents. Men are needed whose early training has been such that the latent originality is not crushed out by a cruel grind at one operation, and the only way this will be accomplished is by giving such as have some ambition a better opportunity to get a fuller knowledge of the fundamental science, art and mathematics of their work. This schooling should not be with the idea of turning out trained investigators, our colleges of ceramics do that, and neither should the purpose of the work be in any way to prepare for a higher education, for this is the great fault of the present high school system. If such a system of education was followed there would not be any less work for the trained investigator. Rather would there be much more. For as the ability of the trained workers increased in like ratio would this ability to do better things create a demand for original wares and glazes. A need would be also felt for a deeper insight into the why and wherefore of the actions and reactions involved in all processes of manufacture. This need of vocational training every day becomes more urgent. Our neighbors across the water have the start of us and something must soon be accomplished ere we are hopelessly outdistanced.

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THE WORKING OF SOME MONTANA CLAYS.

By RICHARD R. HICE, Beaver, Pa.

INTRODUCTION.

Five years ago we one morning found on our tracks a car of clay of which we knew nothing. On examination it proved to be of four varieties, each carefully sacked and marked, the total amount being some fifteen or twenty tons. We found it was billed from some point in Ohio, and we later found it came from one of our customers, the real point of origin being Great Falls, Montana, and that the people sending the clay would be to see us regarding it in a few days.

We naturally took a look at the clays before the parties arrived; and not being impressed with first appearances, we concluded we wanted to be very careful in all pertaining to the matter. On the arrival of the parties we found they came to see us make up the clays into chimney blocks, thinking all we would have to do would be to shovel the clays into a dry pan and take the finished blocks from the machine. We found that arrangements had been made for the erection of a brick plant at Great Falls to make the material needed in the erection of the big chimney at that point, the blocks to be made from the materials in the vicinity, samples of which were in the car we had received. After going over the matter it was arranged we should take them up in our own way, starting with small trials and working up to the finished blocks, if we could make them from the clays received.

The question of whether the samples were fairly representative of the deposits seemed settled, and coming from such a source we felt they were fair, average samples. This phase of the question was, therefore, dismissed at that time, the character and sufficiency of the deposits, as well as their uniformity, being assumed.

It turned out two of the clays were from Field, a point about five miles east of south from Great Falls. The clay marked F Y was called "Field Yellow." It was a rather light yellow, breaking with a sort of flinty fracture, and we got to calling it the "flint clay," a term which has been used for very similar

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clays at other places in Montana. The clay marked F B was called "Field Blue." It was a grayish blue in color, was found intermixed with the F Y clay, the two being irregularly deposited at Field, but normally the F Y belonged on top, the F B grading downward into a softer form. The F B proved exceedingly plastic and altogether too sticky for good working.

The other clays were marked S R and K C. These were both from deposits at and near the location of the proposed plant and near the smelter at Great Falls. The S R clay was bluer than the F B, and at the same time softer, more plastic, or perhaps merely more sticky, than the F B. The K C was a surface clay, found at the location of the proposed plant, and worked near-by by the soft mud process for common brick. Wood was being exclusively used for fuel, and it was locally said no other fuel could be used successfully. This clay was reddish in color, very sandy, and we were advised not to consider it, as it would not form a good substantial body, such as was needed in the erection of a structure over 500 feet high. We, therefore, neglected it entirely in the earliest experiments. Immediately under the K C clay came the S R, which was not used locally.

PRELIMINARY EXPERIMENTAL WORK.

The first trial pieces were made up by hand and, in the absence of all knowledge of the behavior of the clays, were placed in the evening on the top of a steam radiator. In the morning they were dried and sound.

Under all the conditions attending the supply of the clays and the getting of the same to the plant, it seemed desirable that as little of the F Y clay should be used as possible, and we very early concluded it would be better to use a combination of the clays. We found some difficulty in grinding small lots of the F B and S R clays for trials, and finally had to grind them in a dry pan. The grinding was then accomplished with difficulty, owing to the extreme stickiness of the clays and their adhesion to the iron of the pan. The other clays ground readily. All were passed through a ten mesh screen.

A series of trials was made up by hand, being all made nine inches in length, but perforated in about the same proportion

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as chimney blocks. These were made up in the afternoon as follows:

Mark.	Composition.
F B	Made entirely of F B clay.
S R	Made entirely of S R clay.
A	2 parts S R, 1 part F Y.
B	2 parts F B, 1 part F Y.
C	1 part S R, 1 part F Y.
D	1 part F B, 1 part F Y.
E	1 part S R, 1 part F B, 1 part F Y.

The F Y clay was not tried alone as it was not sufficiently plastic.

At five o'clock these were placed in the cool end of the dryer, behind some 30,000 brick made during the day. In the morning they were so badly cracked as to be of no value, although they were run down through the dryer and burned, to get a line on the burning behavior.

A second set of trials was made of the same proportions and bearing the same marks. These were carried to the office and placed at a distance of about 18 feet from a radiator, where there was just sufficient heat to prevent freezing. After 72 hours we reported the condition of the trials as follows:

"Trial A is $8^{1}/_{2}$ inches in length and not over half dry. It shows no sign of cracking as yet. Trial B is $8^{11}/_{16}$ inches in length, not cracked yet, and appears about one-third dry. Trial C is $8^{11}/_{16}$ inches in length, has one large crack in the top edge, while the lower portion is quite soft. This trial as a whole is not over one-fourth dry. This trial is not satisfactory as it seems as if some one must have picked it up and set it down with considerable force, as the bottom edge is badly out of shape. Of course this may be due to the weight of the brick alone. We will make up another trial of this latter to-day. Trial D is not cracked, is $8^{23}/_{32}$ inches long and about one-third dry. FB is $8^{11}/_{16}$ inches long, and still quite soft, not over one-fourth dry and is cracked. This crack may be due to difference in shrinkage as the upper portion of the brick is drier than the bottom edge. Trial S R is $8^{11}/_{16}$ inches long, about one-fourth dry and is cracked. Trial E is $8^{3}/_{4}$ inches long, about one-third dry and apparently still sound."

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We thought we could begin to see where at least some of the troubles would be, and later in the same letter said:

"It would seem to us that drying the brick will be quite a problem. With these plastic clays we would think there would be little difficulty in making the blocks on the machine, but if the material was our own we would have it put up to the dryer man good and stiff as to whether he could dry the material..... We....think at present that the drying is proving quite a problem."

The next day we again reported the progress of the trials, and closed our letter thus:

"We made up yesterday additional trials C and F B. These are still too soft to say anything regarding them so far as shrinkage is concerned. They have been allowed to simply air dry and were placed on wooden pallets on edge. The top edges of the brick seem to have all the shrinkage and there is no shrinkage whatever on the lower edge, which this morning is much softer than when the trials were made yesterday. It would seem that the water has not so much evaporated from the surface as that it has passed down through the clay to the lower portion of the brick, leaving the top stiffer than when made, but the lower portion of the trial with more water than yesterday. This behavior accounts, at least in large degree, for the fact noted yesterday, that some of the trials were all out of shape. This behavior of the water is a very unusual thing, and will complicate the satisfactory drying of the clay, and only emphaszes what we said in our letter yesterday, that if the material was our own we would put it up to the dryer man to dry the clay."

Some of the clay had been sent to the people making the machinery and erecting the plant, including the dryer, and the next day we received a letter from them. They said:

"We would very much like to have you write us giving the results of the tests and stating whether or not there was any difficulty in drying the wares made from each material, also whether they checked or cracked.

"We, too, are making some tests, but unfortunately have not a drying apparatus and have had a little trouble in successfully

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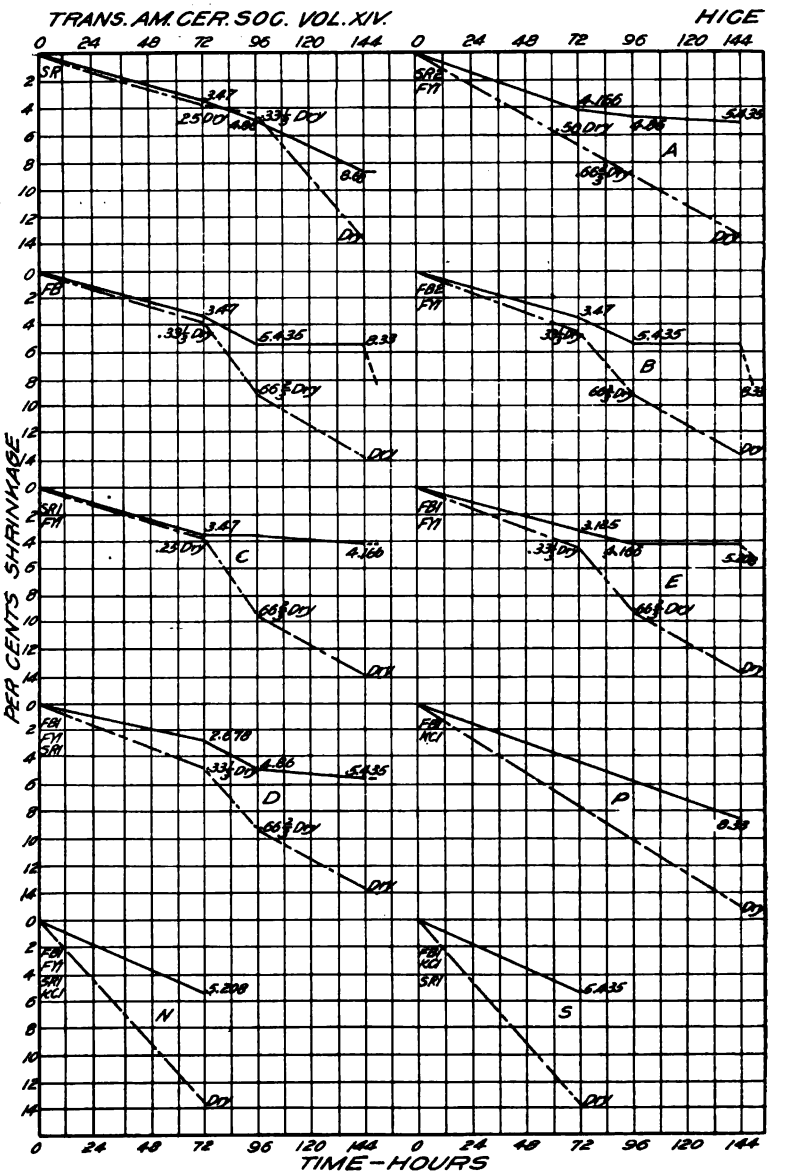

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drying the test blocks. This may or may not mean much, and therefore we are writing you anticipating you will be able to furnish reliable particulars regarding this point."

We did not have the "reliable particulars" and thought the trouble in drying did mean "much."

One hundred and fourty-four hours after making all the trials were dry enough to set, the shrinkage being shown on the diagrams. The diagrams also indicate the shrinkage in burning, and some facts may be noted regarding this. The S R clay seems to have all its shrinkage in the drying, no additional shrinkage being noted in the burning of the trials. This also seems to be the case with two of the trials in which this clay was made up in combination. It is probable, however, that in the S R and C trials the opening up of the drying cracks during the burning offset the burning shrinkage. In the E trial, however, which was sound, no additional shrinkage was noted.

Before this time we had come to the conclusion that if chimney blocks were to be made in Great Falls there would have to be some other material from which to make them. We did not know what might be available and could get no information on this point. The published geological literature was no help, and we considered making a trip there to see what we could find, and if it had been later in the season would probably have gone for this purpose. Under the circumstances, we turned to the K C clay, which we had been advised not to use. This was a residual deposit and quite sandy. We felt we needed something with these clays which would increase the water-holding capacity and prevent the passing of the water downward through the clay by gravity. This passing of the water downward through the clay meant it was not retained in the pores by capillary attraction, and, while the preventing of this movement of the water might not help the drying so far as cracking of the ware was concerned, yet it would at least help to keep the brick in shape during drying, and hasten the drying by exposing a greater water-bearing surface to the air.

After some preliminary experiments we made up two additional sets of trials as follows:

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Mark.	Composition.
N	1 part each F B, S R, F Y, and K C.
S	1 part each F B, S R, and K C.

Also trials of the K C clay itself.

We had sufficient confidence in the drying of these trials to place them at once in the dryer, and two days later reported that both came out sound and that each had but half an inch of shrinkage. We then suggested the making up of the major portion of the clays into blocks, using equal parts of each of the four clays. This was done and after passing through the dryer the blocks were set in a small kiln and burned with all possible care. We spent one day longer than was our practice in the burning of this kiln, and burned it off some six cones below our ordinary burning temperature. Of the top set of cones, 2 was down, number 3 not started. Of the middle set of cones, 1 was about down and 2 not started, and of the bottom set of cones, 1 was just starting. This was certainly all the heat the clays, when used in the proportions given, would properly stand, as was shown by the condition of the blocks when drawn. The resulting blocks were fairly good. Of course many were checked, but they had the strength needed for the work, and we advised the people that the clays as received by us, if carefully worked, would make a fairly good block.

WORK AT THE PLANT.

At or before the time we received the clays the contract had been made for the erection of the brick plant, and while we were experimenting, work was going along in that line. This was, of course, out of our control in any way, but we were expected to take a hand in operating the plant, and accordingly the troubles were transferred to Great Falls about the first of July.

Geology of the Deposits.—Great Falls and the region to the southward and southeastward lies in the lower Cretaceous formation. This was first determined by Newberry in 1887 and has been repeatedly confirmed since. The measures are of fresh water origin as is shown both by the fossil plants and the invertebrates. These measures are known as the Kootenai and have a thickness

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of about 450 feet. They are overlain by the Colorado shales, the Fort Benton of the Meek and Hayden survey.

The Montana lobe of the Wisconsin stage of glaciation approached within a few miles of Great Falls, and blocked the drainage of the Missouri river, creating a large lake, in which we now find characteristic lavustrine deposits. During the time of the interference with the old line of drainage of the Missouri, the waters were forced into a new channel, which has been retained by the present river, just as similar channels have been cut and retained in other portions of the glaciated region.

Fisher[1] has made a short report of the clays at Armitage, near Belt, a few miles southeast of Great Falls, and in his report mentions the clays about Great Falls. There does not seem to me to be much doubt of the approximate correlation of the clays at Field with those at Armitage, although it must be borne in mind that all these formations are exceedingly lenticular and cannot be traced continuously any great distance.

The coals of the Belt region are about sixty feet above the base of the Kootenai. They are quite irregular, but are the best source of fuel within a large region and will continue to produce pretty large quantities of coal even under the relatively unfavorable conditions. About thirty feet above the coal, comes the clay now being worked near Belt. The description of the Armitage clay pretty well fits the F B clay. These are not the underclays of the coal of the region, the coal lying on sandstone or sandy shales. The clay mined by the Anaconda Copper Mining Co. near Belt are plastic, according to the report of Fisher. He says:[2]

"The clay in this mine is light gray to slate colored, fine-grained and uniform in texture. It has a greasy feel and a subconchoidal fracture, and in places indistinct laminations can be seen. Although the material contains all the minerals ordinarily found in clay of this character, the only one which could be detected with the naked eye or a hand lens is pyrite, in crystals most of which are cubical in shape."

[1] U. S. Geological Survey, Bull. No. 340, p. 417.
[2] Loc. cit., p. 420.

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As will be seen later there seems but little common in the two clays when viewed chemically.

Fisher also speaks of the clays at Field and at Great Falls. That at Great Falls is the K C clay referred to above. It is a sandy clay and has been used for the manufacture of common brick by the soft mud process and later with a stiff mud machine. It is about thirty feet in thickness and lies something like three hundred feet above the base of the Kootenai. About five miles south of Great Falls is Field. Fisher says the clay here is at about the same horizon as that at Great Falls. If so there is a very marked difference in the character of the clays, as there seems nothing in common in the deposits. From information obtained from those familiar with the localities, I am inclined to think the Field deposit is somewhat lower in the formation than that at Great Falls. At one time there was a brickyard at Field for the making of fire brick, but this was abandoned some years since. Fisher says this was owing to the high iron content of the clay. Our own experience with these clays does not bear this out, especially so as regards the F Y clay, which is not discolored in any of the trials.

Analyses.—The Armitage clay was sent to St. Louis for analysis, and Fisher also gives an analysis made by the Anaconda Copper Mining Co. Analyses of the Field clays have also been furnished by the Boston and Montana Smelter. There seems to be more difference than was expected.

	St. Louis[3]	Anaconda	F Y	F B
Silica	55.38	53.70	70.90	76.80
Alumina	30.86	27.20	19.90	12.75
Ferrous oxide	0.86	...	...	...
Lime	0.40	...	0.20	0.40
Magnesia	1.03	...	0.15	0.50
SO_3	0.16	...	...	...
Ferric sulphide	2.23	...	...	...
Alkalies	1.30	2.90	...	...
Water at 100°	0.84	...	...	...
Ferric oxide	6.86	5.00	"Fe" 1.10	2.00
Ignition loss	...	10.85	...	...

[3]Evidently burned clay.—Editor.

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The analyses of the Field clays were made in December, 1906, and evidently from the materials sent us for testing.

At one time a clay was worked near Belt forty-five feet above the clays now worked there. Fisher says this clay "is hard, gritty to the touch and breaks with an irregular fracture." An analysis made by the Anaconda Copper Mining Co. is given by Fisher as follows:

SiO_2	77.6
Al_2O_3	12.2
Fe_2O_3	2.3
CaO	0.2

This analysis, it will be noted, is almost identical with the F B clay at Field, and this deposit appears to me to pretty closely correspond with the horizon of the Field clays.

Troubles in Manufacturing.—About the first of July the brick plant was in shape to operate, that is, the buildings were up, the machinery erected, and one kiln built; then the real troubles in Montana began. On arrival on the ground, it was shortly found the sample clays, collected under the direction of trained mineral men, were not typical of the clays; especially was this true of the Field clays. The K C clay was all right, as it was taken from the active workings at the brickyard. There was some stock of the Field clays on hand to begin work, and no examination of the deposits was made at first.

Difficulties at once arose regarding the working in the machine. The plastic clays, both the F B and the S R, were sticky, and it immediately developed they had a wonderful adhesion to iron whenever they came into contact with that metal. The way the clay would stick to the knives of the machine, to the barrel, and to the die was a revelation. In a short time the barrel became so hot the hand could not be placed on it, and the die gave all kinds of trouble. Steam lubrication, water, and oil, all were tried; and it was determined water was the best of the three. The extreme adhesion of the clay to the sides of the machine and to the die caused a very pronounced difference in the rate of travel of the interior of the column as compared with the surface, with a consequent transverse set of strains which necessarily resulted in immediate checking and cracking. Fortunately

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the first trials of the material was in making brick for additional kilns, and not with radial blocks with fifteen cores each. The clay could not be left in the machine over night, but it was found necessary to thoroughly clean out the pug mill and machine every evening. In the morning the polished iron was covered with a thin green coating.

When the column got on the cutting table, more troubles arose. The adhesion of the clay was just as great to the measuring belt as to the iron of the machine, and when the column passed off the belt to the platens of the cutter proper it stuck right there, and a fresh set of troublès arose. The adhesion of the clay to the cutter was finally partially overcome by the use of lard oil—a rather costly lubricating material at a dollar and forty cents per gallon.

As the clay continued to come from Field, it was more and more apparent it could not be depended upon; there was no regularity in the proportions of the F B and the F Y. On inspecting the mine it was seen at once the samples sent us were not typical or fairly representative of the deposit, in fact there was such an intermingling of the different parts of the deposit, and they were so discontinuous, both as regards the deposit as a whole and as regards the two different varieties of the clay, that no set of samples would be fair. Also there was quite a difference in the working of the clay from the different portions of the opening, and it was evident some other source of material must be found if the 16,000 tons of blocks required for the chimney were to be made.

All this time the plant was running with an enormous loss in drying, and with the kilns turning out one-third, and, indeed, more of the brick cracked. About three miles below the smelter, on the other side of the river, a green shale was found, which promised well. This was some two hundred or more feet below the horizon of the K C clay. This, however, like most of the other deposits of the region, was a small lens, which soon ran out, and the plant was back to the old clays with all their troubles. In an attempt to help out the drying one-half was added to the dryer and a warming room was built, into which the brick were run and warmed up in a damp atmosphere before going into the

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dryer. This helped but little with the Field clays or the S R, but was of advantage with the shale and the K C clay.

Our Mr. Stewart, who had been at the plant since the first of July, was called home about this time and did not return for several weeks, when they were back on the Field clays with all their troubles. He had been paying close attention to the working of the plant, relying on what the local people said regarding the shale deposits and their absence. While he was east, we went over all phases of the matter very fully and were convinced the Field clays would have to be dropped, but nothing appeared to take their place. On his return to Great Falls, he found across the hill from the brick plant, where the grading for the flue from the smelter to the chimney was in progress, a large deposit of shale which turned out fairly well.

This shale occurred something like one hundred feet below the horizon of the K C clay. In common with all the deposits of the region, it effloresced badly, but under the circumstances this was no objection so far as appearances were concerned. It did not run very regular in its working, and could be handled with difficulty when but a small portion of the material immediately overlying was present. This was often the case, for the material was loaded with a shovel and, the top being irregular, the overlying material was often mixed with it. At the same horizon at other points this same shale was not found. In drying it was much better than the Field clays, but there was generally quite a loss, unless it was first put through the heating chamber before referred to, although at times it dried well when put directly into the dryer.

Relation of the Clays to Bentonite.—I am not prepared to make any suggestions as to the cause of the drying behavior of these clays. When I first read Orton's paper in the Transactions of the last meeting, I did not have the analyses of these clays at hand; and, his experience being the same as we had with these lower clays, noting the similarity of his clays with Bentonite, and being familiar with the action of the latter, I was inclined to assume the same cause for the similar behavior of these Cretaceous clays. With the analyses before me, however, there does not seem to be any relation to Bentonite. The non-plastic character

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of the F Y clay, with a lower silica and higher alumina content than its associated clay, the F B, seems also rather unusual, as is the high silica content of the plastic F B clay, 76.8 per cent.

The silica and alumina content of the several clays mentioned above and their relation will be better shown by the following table:

	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
SiO_2.....	46.30	55.38	53.70	54.13	68.0	65.24	76.8	77.6	70.9
Al_2O_3.....	39.80	30.86	27.20	19.67	13.5	15.88	12.7	12.2	19.9

a Kaolinite.
b Armitage clay, U. S. G. S. at St. Louis, Fisher.
c Armitage clay, Anaconda Copper Mining Co., Fisher.
d e Orton, Trans. A. C. S., XIII, p. 782.
f Bentonite, U. S. G. S., Bull. 285, p. 446.
g F B clay, Fields, B. & M. C. C. & S. M. Co.
h Armitage clay, Anaconda Copper Mining Co., Fisher.
i F Y clay, Fields, B. & M. C. C. & S. M. Co.

Occurrence of Gypsum.—Another fact that probably needs mention is the common occurrence of gypsum through all the horizons of the Cretaceous and Tertiary of all this region. This is a common ingredient, being scattered in crystals of all sizes, and some were found in the Field clays. The effect of this mineral as reported by Kramm in the last volume of the Transactions of the Society causes this to become a factor in the consideration of any preheating scheme in any attempt to work these clays commercially. As it is found in crysals of some size, it might readily be missed in the collection of small samples, while seriously affecting the clays when taken in large quantities.

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NOTES AND DATA ON OPERATION OF THE DENNY-RENTON DOUBLE DECK TUNNEL DRYER.

By S. C. KARZEN, Akron, Ohio.

INTRODUCTION.

The following is a report, in the form of a series of notes and observations, on work done in the regulation of the tunnel dryer at the Renton plant of the Denny-Renton Clay & Coal Co. The work herein described is really supplementary to that already noted by D. T. Farnham in Volume XIII of the Transactions. The regulation was done on the same dryer but after it had been subjected to a few changes. These will be explained later.

The dryer is fully described and photographed in the volume already mentioned; but for a more complete understanding of the article, I have thought it advisable to give a rough diagram, not drawn to scale, but showing the dimensions of the flues, fan location, etc., of the dryer as it is at present. A Bristol recording pyrometer is located in the fan room. Small iron shutters are located at the pressure fan. By this arrangement, we can control the temperature of the incoming air from the kilns. Opening or closing of the shutters tempers the air to the required value, and the pyrometer shows the results graphically. A large door about 5′0″ x 5′0″ is located at the exhaust fan, leading directly to it. Its use will be noted later. The brick cars in use are the ordinary double decked variety, capable of carrying 500 brick pavers per car. An extra ten are allowed in hacking to cover the dryer loss.

The brick are made of a mixture of shale and sandstone, the proportions of which are kept fairly uniform in the preliminary winning. The clay is very sensitive, tending to check on the slightest provocation. Hence, the most extreme care was required to bring the ware through the tunnels intact.

The original pressure fan, 9′0″ in diameter, was replaced by an 18′0″ fan, and shifted to the exhaust end of the dryer, taking the place of the old much smaller one. Also the location of the exhaust fan was different than the position of the old fan. The desire was now to dry 180,000 paving brick per day as against a previous capacity of 160,000, and the reduction of the dryer loss within the allowable limits of ten brick per car.

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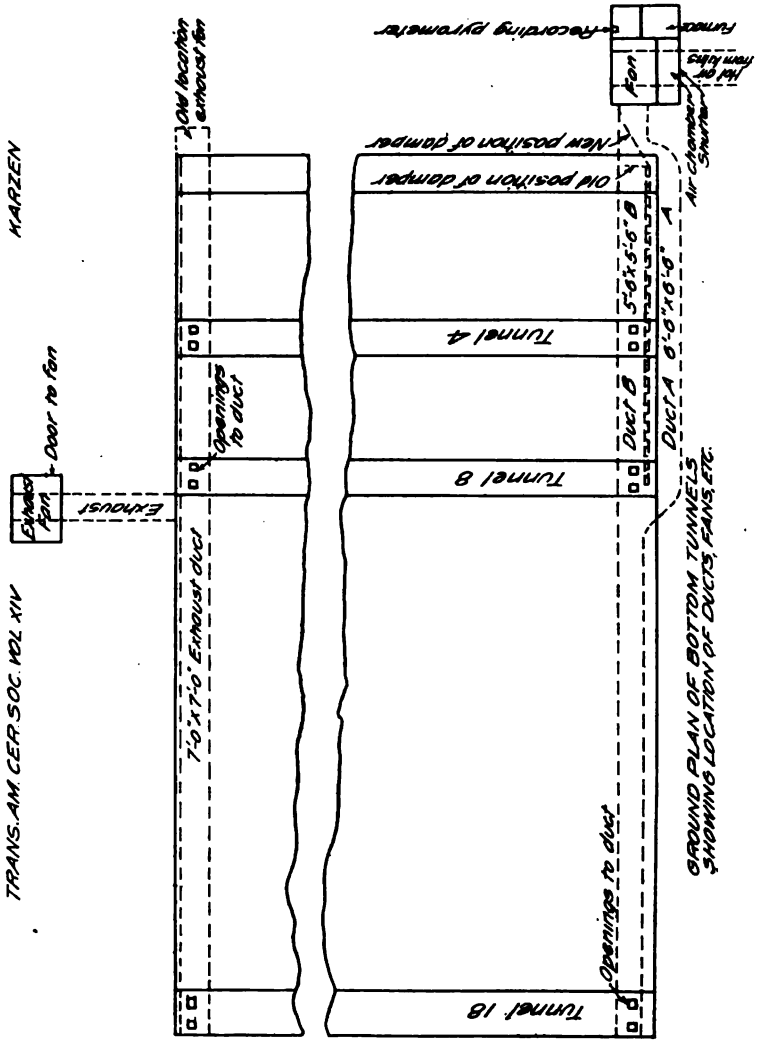

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HEAT DISTRIBUTION AT THE TIME EXPERIMENTS WERE BEGUN.

Before going any farther, I wish to impress upon the reader the fact that this is a double decked dryer, one series of tunnels above the other. At the time this work was begun, conditions were such that more brick could be obtained from the bottom than from the top series of tunnels. Also, the half of the dryer, top and bottom, farthest from the pressure fan received the smallest amount of heat and, hence, gave less dry brick. The top dryer as well as the bottom has eighteen tunnels and will be called T1 to T18. The bottom dryer will be noted as B1–B18. Hence, putting the condition in concrete terms, tunnels B1-B9 were the hottest and gave the most dry brick, and tunnel B10–B19 were next in order; then followed T1–T9, and finally T10–T18. This condition of affairs undoubtedly entailed a loss in heat, and reduced the amount of dry brick which would otherwise have been obtained for this reason.

According to previous experiments on this clay and continuous observations, it had been found impossible to dry the brick in less than three days and still obtain good brick. This meant ten cars of brick from each tunnel per day for the best results. It was found that tunnels B1–B9 would dry twelve cars or more; B10–B18, ten cars; T1–T18, about six cars. The bottom tunnels might have dried even more than twelve cars, but we did not dare draw them. If we had, it would have meant the sending of relatively wet and tender brick into a dangerously hot zone, which meant cracked ware. This consideration prevented us from drawing all the dry brick that could be drawn from the lower tunnels; hence all the heat over and above the amount necessary to dry ten cars per tunnel was wasted. If it could be diverted to the remaining tunnels, it would bring up their output to capacity and thus be used.

PROPORTIONING AIR BETWEEN MAIN TUNNELS.

It follows, therefore, that by proportioning the air in the different tunnels, we could obtain more dry brick and less cracked ware. This was the first step involved in the regulation. Our first

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move was to divert more heat to the farthest tunnels, both top and bottom. This could be done if we could throw a greater volume of air into the duct marked "A." The divisions of air between ducts "A" and "B" was made by the damper "D." Anemometer readings were taken in duct "A" with the damper in various positions until one position directly across duct "B" was found which gave the greatest air volume in duct "A." The rate of drying in the tunnels was noted now for three days. Tunnels T10–T18 and B10–B18 showed signs of doing better, but were still far behind in drying capacity as compared with the remaining tunnels.

One other plan remained, namely, the enlargement of the damper. This was done, and again readings were taken until the best position for the damper was found. After the damper was enlarged, we found that we could throw a greater volume of air into duct "A" than was really desired, and it was by constant experiment and observance of the tunnel drying action that the precise position for "D" was finally determined. The proportion of air volume passing through the two ducts was:

$$\frac{\text{Volume cu. ft. per min. in "A"}}{\text{Volume cu. ft. per min. in "B"}} = \frac{1.6}{1}$$

That is to say, the farther tunnels required a greater air volume than the nearer tunnels to do the same drying because of loss of heat by radiation and reduction of volume due to friction before finally entering the tunnels.

The enlargement of this damper proved beneficial in more ways than one: (1) It allowed us to shift more air to the farther tunnels. (2) It seemed to relieve a certain back pressure on the fan, and hence the fan was able to throw a greater air volume without increase of power. In the old positions of the damper "D," directly across duct "B," the damper obstructed the direct flow of air and caused back pressure on the fan. The new position, which the enlargement enabled the damper to take, removed a considerable amount of this direct obstruction, the air striking the damper at a tangent and gliding off.

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EQUALIZATION OF DRYING IN TOP AND BOTTOM TUNNELS.

Having now distributed the air supply between the farther and nearer tunnels, our next move was to equalize the drying of the top and bottom sets of tunnels.

As described in Mr. Farnham's article, the air for the lower tunnels passed through two openings in the floor of the tunnel, there thus being direct communication between duct and tunnel. On the other hand, the air had to pass upward through ducts in the walls quite a distance before it could enter the top tunnels. The tendency was, of course, for the air to pass into the lower tunnels and completely omit traveling to the upper ones. However, by placing plates over the bottom holes, the air was cut off from the lower tunnels and forced to pass upwards. It was, on the whole, a cut and try method. The anemometer readings were useless. We would cut off a square inch of cross-section in the holes of each of the lower tunnels and note the effect for three days on the drying of the upper tunnels. In this way, little by little, we cut off the lower tunnels, thus forcing the air upwards, until finally the upper tunnels did as much drying as the lower tunnels.

A theoretical method of figuring the necessary size of openings required is here given. The method of determining the exact cross-section of openings necessary is that used by Mr. D. T. Farnham in his flue regulations (see Vol. XIII, Trans. A. C. S.), and it was at his suggestions that the formulae were applied to the following calculation.

(*a*) The large main duct from pressure fan divides into two ducts, A and B, as per diagram:

Duct A = 6′0″ x 6′0″ approximately.
Duct B = 5′6″ x 5′6″ approximately.

To convert a rectangular duct into the equivalent circular duct, use formula:

$$D = \sqrt[5]{\frac{32\,a^3b^3}{\pi^2(a+b)}} \qquad a = 5'6''. \quad b = 5'6''.$$

Solving, we have

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D = 6.059 for duct B.
D = 6.61 for duct A.

2) 12.669
6.33 = average diameter of each.

To find one large duct, equivalent in diameter to both A and B, we use

$$N = \left(\frac{D'}{D}\right)^{\frac{1}{2}} \quad N = 2,\ D = 6.33,\ D' = ?$$

Substituting values and solving, we obtain

$D' = 8.3'_4$ diameter of one duct equivalent to the two.

There are thirty-six tunnels, with two holes per tunnel, which must be equivalent to this large duct. Hence, seventy-two holes. Again using

$$N = \left(\frac{D'}{D}\right)^{\frac{1}{2}} \quad N = 72,\ D' = 8.3,\ D = ?$$

we obtain

$D = 1.485$ = diameter of each hole.

Reducing to rectangular dimensions by

$$D = \sqrt[5]{\frac{32\ a^3b^3}{n^2(a+b)}} \quad D = 1.485,\ a = ?$$

we get an opening 16″ x 16″, two of these per tunnel.

The cross-section of the exit duct is 7′0″ x 7′0″. We first reduce to diameter, then figure this into seventy-two round holes, and finally into square holes 15″ x 15″.

As stated further in the report, some of the holes had to be reduced in size. Theoretically, therefore, to keep our area equalized, it would be necessary to increase the farther holes. In other words, whatever cross-section was cut off holes at one end had to be added to the cross-section of the holes at the other end in order to keep the total cross-section equivalent to the main ducts.

PLAN OF FURTHER WORK.

Having now done all that was possible with the dryer under the existing conditions, we mapped out a course of action something as follows.

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To increase the capacity of a dryer:

- Increase in quantity of dry brick.
  - Increase in quantity of air.
    - (1) Increase h. p. of fan (speeding).
    - (2) Increase size and smoothness of ducts.
    - (3) Increase tightness of walls.
    - (4) Decrease length of ducts.
  - Increase in temperature of air.
    - (1) Heat from kilns (more kilns).
    - (2) Furnace to aid kilns.

Taking up consideration of these items in the order named:

Increase in quantity of air.

(1) Increase h. p. of fan. The fan could be speeded up within certain reasonable limits. The limiting conditions would be: (*a*) too high for velocity for economical usage; (*b*) extreme danger of air checking cooling brick from too rapid cooling.

(2) The size and smoothness of ducts are constant quantities and cannot be changed.

(3) The tightness of wall is a constant quantity.

(4) The length of duct is a constant quantity.

Increase in temperature of air.

(1) At the time no more heat except as might be had by speeding of fan could be had.

(2) The use of a furnace was to be avoided, if possible.

REGULATION OF QUANTITY AND TEMPERATURE OF AIR.

Before proceeding further, the theoretical air volume required was figured from the following data:

Required to dry 180,000 pavers per day.

Average weight, wet, 3.785 kgms. Iron cars 350 lbs.

Average weight, dry, 3.265 kgms. 500 brick per car.

Average brick temperature, 60° F.

Average outside temperature, 60° F.

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Hot end temperature, 240° F. (This was an assumption based on previous work.)

Cold end temperature, 90° F.

Saturation of outside air, 90%. Saturation desired in outgoing air, 90%.

The calculation was made according to method followed by Minton in his dryer problem (Trans. A. C. S., VI, page 269). The result obtained was 100,000 cu. ft. per minute. Practically, however, we found this far from the true amount. We may account for this, perhaps, by the fact that the temperature eventually used was not continuously 240° F.

The following method was used to determine the air volume required. For several weeks, the temperature at the fan was kept at 220° F., as registered by pyrometer, and the volume of air increased every three days. The condition of brick drawn was noted. For several weeks the same was repeated, only using 230° F. at fan. For several weeks the same was repeated only using 240° F. at fan. The temperature was easily kept constant at the fan by the use of the shutters before mentioned. The increasing air volume was more difficult to attain. When air volume was to be increased, more kiln openings were put on the dryer. When this gave out, the furnace was fired up.

The following conclusions were drawn:

(1) With 220° at the fan and the air supply varying from 105,000 cu. ft. per minute to 130,000, it was impossible to dry 180,000 pavers per day. Beyond this amount, we did not think it necessary to increase our air supply since it meant much cracked ware.

(2) With a temperature of 230° F. at the fan, we would require about 130,000 cu. ft. per minute or better the majority of the week to dry the brick.

(3) Our best results were obtained with a temperature of 240° F. and about 125,000 cu. ft. per minute the first few days, and increasing to 130,000 cu. ft. per minute the latter part of the week.

The original speed of the fan was 125 revolutions per minute. This was, we found, not enough to throw the air necessary by about 12 per cent. Hence, it was necessary to speed it up to 140 revolutions per minute, which gave us all the air we needed.

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Of course, the volume of air thrown by the fan depended a great deal upon the kiln openings on the dryer. Under the old speed, we never could get enough air to dry the brick irrespective of the number of kilns on the dryer. With the new speed, there was often a tendency for too much air to be thrown. Our remedy when this occurred was to reduce the size of the kiln openings on the dryer. There were several direct benefits which the speeding of the fan gave us: (1) The increased air volume that was a necessity in order to dry the brick. (2) The increased speed enabled us to draw heat from the farthest kilns, which had heretofore given very little heat to the dryer.

A good means of regulating the air volume from the kilns would have been the use of a large damper in the main duct leading to the fan. If the air volume should be in excess of what was required, this damper could be dropped until the fan would be throwing the necessary amount. An air gage is a prime necessity where good regulation is desired. It should be a recording pressure gage, placed in the duct leading from the fan to the dryer, and should read air volume direct.

An attempt was made to determine the relation between air volume thrown by fan and the area of kiln opening on dryer, but no definite results could be obtained for several reasons. The amount of air drawn from the different kilns was proportional to their distance from the dryer. Atmospheric conditions caused the amount to vary from day to day. The temperature of the cooling kilns also affected the volume of air drawn from them, irrespective of size of opening.

A sliding scale of air volume and temperature was suggested; that is to say, when air supply became very low, use extremely high temperature and *vice versa*. To a limited extent, this is possible, but there are extremes which can not be used. (*a*) With a small air volume and high temperature, it is possible to so heat the tunnels as to make it impossible for the men to work. (*b*) With large air volume and low temperature, we strike another difficulty. The large volume of air which of necessity must pass through small openings is propelled at so great a velocity as to be carried far down the tunnel before any drying occurs. As a result, the heat carried down the tunnel does less

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drying, is less saturated, and tends to crack the incoming wet brick. These physical difficulties make the sliding scale of air and temperature a difficult system to use. What approximated this sliding scale was finally adopted, but from entirely different reasons.

CONTROL OF CHECKING.

Now that we have gained an idea as to proper amount of air and temperature required to give us our capacity, the next point was to stop the checking.

Manipulation of Covers for Exhaust Holes.—In the cold end adjustment, our primary object was, of course, to obtain a nearly saturated condition; that is to say, from 90 to 95 per cent. saturation. The saturated air from the tunnels was removed through openings in the floor leading to the exhaust duct and so on out to the fan. The exhaust arrangement is, therefore, similar to that used for the admission of the heated air. These openings at the rear end of the tunnels were fitted with covers which could be slipped back and forth. The closing of these holes, of course, acted as a damper on the suction, restricted the speed of the air through the tunnels, and hence helped produce saturated conditions.

The use of these was all very well, but they did not cure by any means. Although the holes were cut down to such an extent as to cause the steam to blow out under the doors, still saturated conditions were not obtained, and the brick still cracked. There were two causes for this. (1) The pressure fan was throwing so great a volume of air. (2) The exhaust fan was traveling at a speed of 150 revolutions per minute, which was in excess of what really was required under normal conditions. Yet this speed could not be cut down, because very often water in the hot air ducts raised great quantities of steam in the tunnels. These two conditions led to the result that the air would be drawn too rapidly into the tunnels, over the cars, and out, dry and unsaturated. This meant that the air was not doing efficient drying, besides cracking the wet and tender ware to a great extent. As noted, no matter how small we made the holes, this was not cured. We, therefore, reduced the size of these rear openings to the smallest possible dimensions that would not

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produce blowing of steam under the doors. Further regulation was done at the exhaust fan.

Regulation at Exhaust Fan.—As stated before, a door 5′0″ x 5′0″ was cut into the exhaust fan house, leading directly into the fan. By opening this, the fan could be made to draw in the outside atmosphere, and in this way suction from the tunnels could be reduced. Hence, though the same volume of air be admitted at the heated end, we were able to control the speed with which it traveled through the tunnels, by means of this door. As will be explained later, Monday, the day on which the brick were dryest, the door was opened widest, and slow reduction of opening took place toward the latter part of the week. We found by experiment that:

(1) About 18″ x 5′0″ was necessary on Monday, Tuesday and Wednesday.

(2) About 9″ x 5′0″ was necessary on Thursday and Friday.

(3) Complete closing was necessary on Saturday and Sunday. By this means we were able to materially help conditions in the tunnels, although it did not totally remedy matters.

Temperature Regulations.—As already stated, it was found that with a temperature of 240° and a volume of 125–130,000 cu. ft. per minute, we could dry 180,000 brick per day. It was, however, impossible and impractical to keep this temperature and volume the entire week. On Monday morning, since the brick had had an extra day of drying over Sunday, we were forced to cut our temperature way down or suffer from excessive cracking. The reason is obvious. The bricks become dry quite a distance into the tunnel, due to two days drying. Now, if we had the normal temperature, the drying capacity of the air is far in excess of the moisture to be expelled. As a result, the air comes to the exhaust end hot and dry. Any wet brick which may enter the tunnel come into this hot dry air, fail to get their preliminary steaming, and consequently check badly. It behooved us, therefore, to reduce the temperature and air volume to such an extent as to just take care of the moisture to be expelled.

Our method of procedure was as follows: Saturday evening, after the last dry brick had been drawn from the dryer, the temperature was immediately reduced to 230° F. and so kept until

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Monday. Conditions in the dryer were noted Monday. The same was done the next week reducing to 220° F., and finally to 180° F. In each case as much as possible of the air volume was cut down likewise. We hoped in this way to do only one day's drying in the two; that is to say, have the brick in the same condition Monday morning as if they had been subjected to only one normal day's drying. By reducing the temperature as stated to about 180° F. and the air volume to about 100,000 cu. ft. per minute, we obtained these results.

Of course we could not immediately increase the temperature and air volume Monday morning, but did it in stages. Monday morning the temperature was raised to 200° F., with the air volume about 110,000 cu. ft. per minute. Monday evening the temperature was 210° F., then 220° F. at midnight, and 230° F. about Tuesday morning; 240° F. and the full air volume was obtained as soon as the brick warranted it. Of course, the condition of the brick would show how rapidly the temperature should be raised. If they began to show wet spots early, the temperature was raised more rapidly. When we obtained 240° F. and about 130,000 cu. ft. per minute, we were reasonably sure of dry brick up to the capacity of the dryer. In this way we prevented a weekly dryer loss on Monday morning.

Baffles.—With all these precautions, we found great difficulty in keeping our dryer loss below the limit assigned, ten brick per car. It was found that the top course was the one most troubled. We, therefore, calculated on the following conditions. The air, of necessity large in volume, swooped in through a small opening at a high velocity. It shot up to the roof of the tunnel and stayed there, the natural tendency of hot air to rise keeping it there. The hot air traveled down the tunnel, hugging the roof, drying the upper courses, and never getting its full quota of moisture. It came to the rear far from being saturated and very hot. The result was poor drying and cracked brick. Our problem was the forcing of this heated air down among the brick, where more efficient work could be done.

A number of so-called baffles or curtains were made. These consisted of heavy canvas, 18″ wide, suspended on rods and placed the full width of the tunnel. They were so placed that the canvas

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would just drag over the tops of the cars without pulling off any brick. Beginning at the rear of the tunnels, these curtains were placed two car lengths apart, from three to four baffles being used in each tunnel. The result was instantaneous. The air striking these baffles was diverted downward, gathered its full quota of moisture, and was withdrawn from the rear end in an almost saturated condition. Another method, similar in principle to baffling, was the raising of several brick above the level of the remaining brick. These acted as a screen to the remaining ware. This was not nearly as efficient as the curtains.

Drying of Blocks.—We very often had an order of blocks to dry. For awhile we attempted to dry these at the same rate as the smaller shapes but with very poor results. However, by the closing up of the hot end openings and thus drying the blocks much more slowly at a lower temperature, we obtained very good results.

SUMMARY.

CONDITIONS IN DRYER NECESSARY FOR BEST RESULTS.

Day	Air, vol., cu. ft. per min.	Temp., degrees F.	Exhaust fan: Rev. per minute: Winter	Exhaust fan: Rev. per minute: Summer	Exhaust fan: Door opening	Rev. Pressure fan, per minute	Tunnel	Dimension exhaust opening	Dimension hot end opening
							T 1	3½″ × 12″	Full
							2	3½″ × 12″	Full
							3	3½″ × 12″	Full
Mon.....	125,000	200°	150	125	5′0″ × 18″	140	4	3½″ × 12″	Full
		210°					5	3½″ × 12″	Full
							6	3½″ × 12″	Full
		220°					7	3½″ × 12″	Full
Tue.....	125,000	230°	150	125	5′0″ × 18″	140	8	3½″ × 12″	Full
		240°					9	5″ × 12″	Full
							10	open full	Full
							11	open full	Full
Wed.....	125,000	240°	150	125	18″	140	12	open full	Full
							13	open full	Full
							14	open full	Full
							15	open full	Full

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CONDITIONS IN DRYER NECESSARY FOR BEST RESULTS (*Continued*).

Day	Air, vol., cu. ft. per min.	Temp., degrees F.	Exhaust fan: Rev. per minute: Winter	Exhaust fan: Rev. per minute: Summer	Exhaust fan: Door opening	Pressure fan, Rev. per min.	Tunnel	Dimension exhaust opening	Dimension hot end opening
Thu.....	130,000	240°	150	125	9″	140	16	open full	Full
							17	open full	Full
							18	open full	Full
							B 1	3½″ × 12″	5″ × 9″
Fri.....	130,000	240°	150	125	9″	140	2	2½″ × 12″	5″ × 9″
							3	2″ × 12″	6″ × 8″
							4	2½″ × 12″	5″ × 9″
							5	3″ × 12″	5″ × 9″
Sat.....	130,000	240°	150	125	0″	140	6	3″ × 12″	5″ × 9″
							7	3″ × 12″	6″ × 8″
							8	3″ × 12″	6½″ × 8″
							9	3″ × 12″	7″ × 8″
							10	3″ × 12″	7″ × 12″
							11	3″ × 12″	7″ × 12″
							12	3″ × 12″	7″ × 12″
							13	3″ × 12″	7″ × 12″
							14	3″ × 12″	7″ × 12″
							15	4″ × 12″	7″ × 12″
							16	5″ × 12″	7″ × 12″
							17	6″ × 12″	7″ × 12″
							18	6″ × 12″	7″ × 12″

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Mr. Ellis Gates: This is a very interesting paper, for several reasons; the two most important ones, it would seem, are as follows:

First: It shows that no matter how carefully calculated the construction of the dryer and distribution of hot air may be, it is still necessary to adjust the dryer by practical experiments.

Second: The manner of adjustment is quite interesting and will no doubt prove to be of interest and profit to others who wish to get greater efficiency from their dryer.

It, however, seems strange that "bafflers or top curtains"

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were not tried at first, inasmuch as they have been used for many years in tunnel dryers, it being necessary to have some arrangement for throwing hot air to the bottom.

It would seem that an auxiliary fan located midway between the large intake fan and the further kilns would overcome the difficulty in securing air from the further kilns. This fan would need to be run only when cooling one or more of the distant kilns.

Mr. Burns: Mr. Karzen has given a full history of the changes that were made in the dryer in order to bring its capacity from 160,000 to 180,000 brick per day. There are a few points, however, in his observations with which I take issue.

Under the discussion head "Regulation of Quantity and Temperature of Air," another means of regulating the air volume from the kilns has been suggested instead of placing a damper in the main duct, namely, to cut a hole in the duct between the fan and dryer and to have it controlled by a shutter or weighted lid which, when opened, allows excess air thrown by the fan to escape to the atmosphere without going through the dryer to the exhaust fan. The advantages claimed for such arrangement are:

First: A better and much easier control of the volume and temperature of the air passing through the dryer during the first part of the week, when lower temperature and less volume are desired, irrespective of excess number and temperature of kilns connected to the waste heat system.

Second: Cooling kilns that have to be cooled within a certain time limit in order to take care of the dryer's output would not be held back because only a limited amount of air may be drawn from them on account of the conditions existing within the dryer.

"A sliding scale of air volume and temperature (*b*)." A further effect that a large air volume and low temperature has on the brick in a tunnel is that a thin dry crust is formed on brick part way down the tunnel, due to high air volume and too low temperature to sweat the brick. Checking takes place for a considerable distance down the tunnel as well as at the extreme back, due to the too rapid shrinking of this outside crust.

"Manipulation of Cover for Exhaust Holes:" The figures

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of 90 per cent. and 95 per cent. saturation are a little low. Ninety-five per cent. to 98 per cent. has been found, from the daily reading of the wet and dry bulb thermometer, to give better results. Almost invariably the best results have been obtained when the difference in temperature has not been over 4° F., preferably 2°, and when the temperatures have been within the limits of 82° to 88° inclusive, conditions generally being the best when the wet bulb shows 84° and the dry 86° F.

"Regulation at Exhaust Fan:" Another device adopted to aid in the control of the air at the exhaust fan is by means of a damper 3′ x 7′, placed on top of the exhaust fan stack, which is raised and lowered as conditions in the dryer seem to warrant. This is supplementary to the 5′ x 5′ door leading directly into the fan.

As Mr. Karzen has stated, air and temperature have to be regulated as conditions of the brick in the front and back of the dryer seem to warrant, changing them somewhat from any set of regulations in regard to amount and temperature of air for successive days of the week, but on the whole conforming quite closely to them.

In case a double deck dryer was to be constructed for as sensitive shale as the one under discussion, a general improvement might be obtained by building single track tunnels, allowing the least possible clearance space for the cars within the tunnels, both on the sides and overhead. Such a dryer would require a solid foundation, which the dryer under discussion has not, as the whole plant is located on a fill made by the Cedar River when it made one of its periodical changes of course. The construction of the dryer itself would have to be thoroughly rigid in order to keep the tunnels and tracks in perfect alignment. In such a dryer baffles would not be necessary and with less clearance all around the car, the air would be forced through the brick more evenly, requiring less air to do the drying more efficiently.

Mr. Karzen: The suggestion made for another means of regulating air volume from the kilns, other than a damper in the main air flue, undoubtedly has the advantages stated in the discussion. It has, however, the disadvantage of allowing

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a considerable loss of heated air which would otherwise have been retained in the kilns. Where this latter consideration is unimportant, the method just suggested would be the best. In the present instance, however, it has often been found necessary to increase the hot air supply by means of a wood-fired furnace. Hence, in order to waste as little heat from the kilns as possible, the damper in the flue should be used.

Ninety-eight per cent. humidity is a dangerous figure to use, for the reason that it too closely approaches completely saturated conditions. If your tunnel shows a humidity of 98 per cent. about the middle of the week, you can undoubtedly expect complete saturation before the end of the week is reached. This means a considerable loss, due to dripping of moisture or even softening of the ware. I believe that for average safe conditions, 95 per cent. is best.

Any scheme, the use of which would prove an aid in retarding the suction of the rear fan, is good, and the one mentioned must undoubtedly be a great help.

The use of baffles, I think, would be beneficial even in the most closely built tunnels. Several of the tunnels had very low roofs, but still gave poor drying conditions until the baffles were used. No matter how long or how closely built a tunnel is, the tendency of the heated air is to rise, and, therefore, some means must be used to force the air downwards at intervals.

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THE POWER CONSUMPTION OF STIFF-MUD BRICK MACHINERY.

By RICHARD R. HICE, Beaver, Pa.

INTRODUCTION.

One of the problems in connection with the equipment of any clay-working establishment is that of power, and this is perhaps more important in stiff-mud brick plants than in other branches of the clay industry. When we examine the catalogues and literature issued by the various manufacturers of brick-making machinery, nothing is more marked than the absence of any information, at least of a reliable character, concerning the power needed. The fact that there is a wide difference in the ideas of different machine people as to the power required by machines, of supposedly the same capacity, is shown by the difference in the diameter, width of face and speed of the pulleys ordinarily used. It must be admitted that machines of practically the same capacity, differently proportioned, will require in some cases somewhat different power equipment. This, however, is by no means so true of some classes of machinery as of others.

In the case of dry pans we should not expect much difference in the power consumption in grinding, say, the material for twenty-five hundred bricks per hour in pans of different makes, using the same clay. It is to be granted that different clays may require different amounts of power, even when the capacity of the pan may be the same. One clay may be quite hard but drop readily through the screen plates, another may be quite easily crushed, but, owing to physical conditions, arches over the slots in the screen plate and does not so readily pass out of the pan. In such cases there may be quite a difference in the power consumption. On the other hand, where the same clay is used in pans of different makes and different proportions of weight of mullers, width of face, and arrangement of slots in the screen plates, there may be considerable difference in the power consumption, but if the arrangement of the screen plates is such as to allow the material to pass through readily there should be but

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little difference in the power consumption of different makes of pans.

In the matter of pug mills there is a marked difference in the power consumption, due to the amount of pugging given the clay and not to the difference in shape and "set" of the knives, as generally assumed.

In auger brick machines (turning out the same number of bricks per hour, of the same clay, screened to the same fineness and pugged the same) there is certainly but little difference in the power consumed where the brick are the same density. There is in practice a very marked difference in the density of brick made on different machines, the shape and proportion of the barrels, size and character of the auger and die, being designed to produce brick with perfect corners and reasonably free of laminations, and not of any fixed density. This difference in the column is shown in the difference in shrinkage of bricks made of the same clay, ground and pugged the same, when made in different machines. The density of the burned brick may be practically the same, notwithstanding the difference in the column as it comes from the die.

In all the foregoing generalizations, no consideration is, of course, given to the matter of internal friction of the machine itself, or to the fact of more friction between the moving clay and the machine in one case than in another. These are factors that are largely constant and which, if considered, mean a consideration of particular makes of machines. In the case of auger brick machines, it can be stated as a general rule that the denser the column the more friction between the clay and the machine to be expected, and this is true regardless of the proportion of the machine barrel, or the shape of the knives and dies.

It is the object of this paper, not so much to point out how much power is required for any particular machine, but rather to show the relative amounts of power required by a particular plant operated by a fairly good steam installation, and by the same plant when rebuilt after a fire and operated by electricity. It is recognized, of course, as suggested in the foregoing statements, that these figures should not be used quantitatively with some

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other material; but it is believed the results will hold relatively good in all cases.

STEAM PLANT INSTALLATION AND POWER CONSUMPTION.

This plant, as ordinarily designed, was equipped with an 18 x 42 Corliss engine developing 175 h. p. The material used was a low grade of fire clay from the lower Kittanning vein, relatively hard to grind and screened rather fine. The power was taken from the engine to a line shaft, from which the machinery was all driven. The dry pans, pug mills, and brick machine were driven by belts, and the elevators by rope drive. Owing to the occasional coincidence of the peak loads on the several machines, it was not an uncommon thing to have the engine overloaded several times a day; and to take care of these peaks it was necessary to maintain the full steam pressure constantly, whether any of the machines were temporarily out of use or not. A somewhat careful estimate of the power developed at the boilers for one thousand bricks shows it would run from 75 to 82 h. p. hours.

In common with the usual experience for plants, this one went up in smoke; and in rebuilding it was decided to abandon the steam plant, equip with motors and purchase the current. With the actual cost this paper has nothing to do. In designing the equipment, we found that we had but little data on which to go, and it was determined finally to equip as follows.

ELECTRICAL INSTALLATION AND POWER CONSUMPTION.

Nine foot dry pans are driven by belt from 35 h. p. 60 cycle, 2 phase, 220 v., squirrel cage type, motors, running 560 r. p. m. The shaft of the motors used was very heavy, and they were equipped, therefore, with an overhanging pulley, no outboard bearing being needed. These have now been in use for six months and are entirely satisfactory.

The elevators are driven by independent, $7^1/_2$ h. p., 60 cycle, 2 phase, 220 v., squirrel cage type motors. These motors are, of course, larger than the load seems to require; but they are belted directly to the elevator, no clutches being interposed, and, therefore, the starting torque is very heavy, having the dead elevator, which is about 50 feet in height, to start. There

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is an independent lead line for each dry pan and elevator motor.

The brick machine and pug mill are independent, but both are driven by the same motor. This is a 75 h. p., 60 cycle, 2 phase, 220 v., squirrel cage type, motor, running 570 r. p. m. In this motor, the shaft is extended on each end and equipped with pulleys, one of which drives the brick machine and the other the pug mill. This has proven quite satisfactory as the pull on the bearings is largely balanced by this arrangement and there is no necessity for outboard bearings.

The clay from the screens is carried by a belt conveyor to the pug mill, which is driven by a 3 h. p. motor, using a belt drive. The pump for water supply is also driven by a 3 h. p. motor, and the D. C. generator, which develops the current for operating the drills in the clay mine, is driven by a 5 h. p. motor. A 3 h. p. motor is also used to drive the small machine shop in connection with the plant.

The switchboard is arranged in two circuits, one of which carries the dry pans and elevators; and thus the current consumed in the grinding and elevating is at all times measured by itself. A second circuit carries the brick machine and pug mill motors, also the dust conveyor, D. C. generator, and machine shop motors, so that the reading of the meter on this circuit is more than the brick machine and pug mill proper. The light circuits are entirely independent.

The brick machine and pug mill motors, and the dry pan motors are all equipped with overload and low voltage release, a feature which seems quite valuable when making installations of this character.

The average power consumption for the production of 1,620,700 brick was 30.4 k. w., or 40.75 h. p. hours, per M. brick. Something over one-half of this was consumed in grinding, the average power consumption per M. brick of the dry pans and elevators being 16.8 k. w. (22.52 h. p. hours) while that of the brick machine, pug mill, conveyor, pump, D. C. generator, and machine shop was 13.6 k. w. (18.23 h. p. hours) per M. brick. These average figures of power consumption per M. brick compare very favorably with the power necessarily provided by the steam plant, being less than 60 per cent. of what the steam plant provided. This

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is due to a considerable degree to the fact that during every small shut-down of a machine it is necessary that the steam be kept up in the boilers and that the rest of the plant including all shafting be kept in operation, and in cases where but a small portion of the plant is in operation the entire dead load of engine, shafting, etc., must be carried without any return. When using electricity, with independent motor drives, the power consumption is cut off with the machine. These savings are, of course, obvious to any one.

In our own case, we buy the current, and hence there is no necessity of providing for the peak load as would be the case if we were using steam or if we were generating our own current in any manner. It is not intended to suggest that where one is using electricity and generating his current he could reduce the size of the power plant as indicated by the difference of power consumption shown by the foregoing figures.

CONCLUSIONS.

Few of us probably realize the real cost of our steam power, and even where electricity can be bought at a reasonable rate, most are inclined to think it much more expensive than their old steam plant. There is necessarily a great variation in the cost of power at various plants, due to ever changing conditions; but it would seem safe to say that the power consumed in most stiff-mud brick plants really costs 75 cents to $1.00 or more per M. bricks. The cost of current where it is bought also varies greatly, and an average rate would probably be a mere guess. With the power consumption indicated, 30.4 k. w., at a rate of 2 cents, which would probably be high for the amount of current used and the character of load, the cost of the power per M. bricks would be 61 cents. What the current would cost if generated at the plant depends, of course, upon the amount of power needed and the character of the equipment. It is needless to say that in small plants there would not be much, is any, saving in generating its own current. These are features that must be determined in each particular case.

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DESIGN OF AN ECONOMIC FURNACE FOR TUNNEL DRYING.

By S. C. KARZEN.

The majority of brick plants at the present time use continuous tunnel dryers, the drying being accomplished by waste heat obtained from the kilns. It happens very often that the waste heat is insufficient to do the necessary drying, in which case an accessory in the shape of a furnace is a necessity. It is for such systems that this furnace can be used.

The furnace, as designed, is intended to burn cord wood in 4'0" lengths. The design can easily be changed and the grate area reduced where any other fuel is to be used.

The ordinary furnace is one which obtains the air necessary for combustion from the atmosphere through the ash pits. This, of course, means the heating up of air from atmospheric temperature to a temperature at which it can be used in the dryer. The furnace here shown is designed to utilize the waste heat passing through the duct to support combustion. Since the air passing through the duct is already at a temperature closely approaching the required temperature, only a small amount of fuel is necessary to raise the temperature to the required point.

Generally, furnaces of this type are placed very close to the fan house, the suction of the fan furnishing the draft. In this case, the furnace is connected to the fan direct by means of an asbestos covered tube. The furnace is placed, as shown, directly over the waste heat air duct, having two openings leading directly to it. Receivers, closed at one end and open at the other, are placed over these holes so as to guide the air to the spot where it proves most efficient.

The suction of the fan, now acting as the draft, draws the air up through these receivers into the ash pit and up through the grate bars, thus furnishing the air for combustion. The gases then pass on through the checker work, for better mixing of air with volatile unconsumed gases, into the combustion chamber where final combustion takes place. The products of combustion plus the heated air then pass into the fan through the tube.

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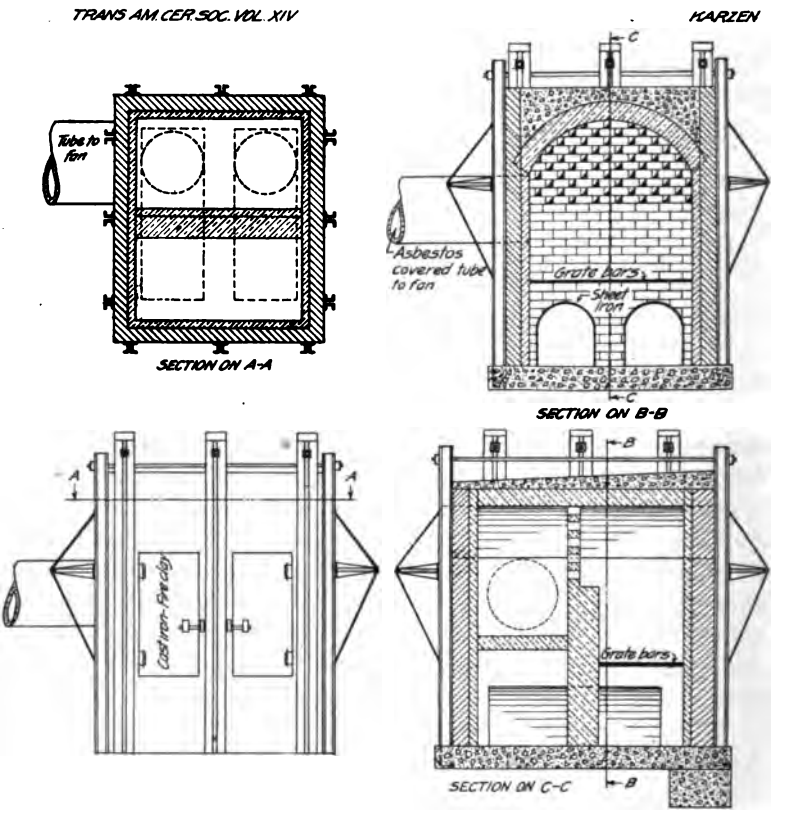

The tube itself may be dampered. A damper can be placed in the large air duct also. By manipulation of these dampers, the draft may be increased at will in either the air duct or through the furnace. An iron damper may also be placed over each hole connecting the furnace and duct, in case it should be found that the cross-section of openings are too great. No trouble should be encountered in forcing the air up through the furnace if these dampers be in place.

The dryer will suffer to a certain extent, perhaps, from soot and smoke. But the combustion chamber and checker work should cure this to a certain extent, and the fuel itself would

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not be fed in such great quantities when using such a furnace as would otherwise be required.

The furnace has never been tested. As stated before, it was merely the idea involved that, I hope, will prove of benefit.

DISCUSSION WRITTEN AFTER READING THE PAPER.

Mr. Burns: The efficiency of such a furnace would depend upon the success which would be met in inducing the fan to draw the air from the main tunnel through the asbestos-covered tube.

The friction which the fan would have to overcome in this comparatively small tube would be a big handicap. To overcome this in the comparatively short distance between the outlet at the fan and the intake in the top of the waste heat duct, the large damper would probably have to be lowered to such an extent that the control of the air supply for the dryer would be materially affected.

The effect of opening the furnace doors would also affect the efficient working of such a furnace. Doors of considerable size would be necessary to handle cord wood, and these would have to be opened very frequently when any considerable heat had to be supplied by this means as not infrequently happens when it is necessary to use a furnace at all. The effect of opening the doors would be to change the air supply from the dryer duct to the outside atmosphere, which is what the furnace is especially designed to prevent. Any cracks in the furnace would tend to destroy the efficient working of such a plan. On the whole, the efficiency and practicability of such a furnace is very questionable.

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A NOTE ON THE ACCIDENTAL PINK DISCOLORATION OF A WHITE ENAMEL FOR TERRA COTTA.

By DUANE F. ALBERY, Terra Cotta, Ill.

Description of the Trouble.—At Terra Cotta, Ill., in the spring of 1911, we ran into an interesting color phenomenon. For some months previous to this time we had been using an enamel of the following formula:

$$\left.\begin{array}{l} 0.148\ Na_2O \\ 0.104\ K_2O \\ 0.443\ CaO \\ 0.087\ MgO \\ 0.218\ ZnO \end{array}\right\} \quad 0.320\ Al_2O_3 \quad \left\{\begin{array}{l} 2.987\ SiO_2 \\ 0.087\ B_2O_3 \\ 0.136\ SnO_2 \end{array}\right.$$

This enamel had been burning to a good white color. The burning was done with coal, about 95 hours on fire, 90 hours cooling. In June, 1911, the fuel was changed from coal to fuel oil, and the time of burning was shortened to 75 hours on fire, 90 hours cooling. At about this time it was noticed that some of the enamel showed a decided pink color. Not all of it, just an occasional piece of terra cotta here and there showed this tint and the color was more pronounced in some cases than it was in others. It was not confined to any one kiln, nor to any special part of the kilns.

Correction of the Trouble.—I could find no reference to anything of this sort either in Seger's works or the Transactions of this Society. My first suspicion was that some peculiar conditions in the kilns were responsible for the trouble. But, at the same time, I realized that there must be some chemical combination, having a pink color, forming in the enamel.

As to impurities in any of the materials used to manufacture the enamel, the following conditions existed: No new supply of any of these materials, excepting tin oxide, had been purchased since some time before the pink color made its appearance. Two samples of tin oxide from the manufacturers were tried out in the enamel. Both of these oxides were rated as A–1, and in both cases the enamel came pink. So, if any impurity in the materials used was the cause of the pink color, this same impurity was present when the enamel was burning to a white color. If the impurity was in the tin oxide, it would be found in the best tin

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oxide we could obtain from the different manufacturers, and we could not, therefore, look for relief in that direction.

In April, 1911, we started burning some terra cotta which had a light pink slip on it; the pink color was produced with a "chrome tin" stain. It was considered possible that some chromic acid had volatilized from this slip and caused a chrome tin combination in the enamel, thus producing the pink color. The high lime content of the enamel would seem conducive to such an occurrence. Messrs. Purdy and Brown, in their article on "Chrome Tin Pinks," in Volume XI of the Transactions of the American Ceramic Society, state concerning stains that in changing from a high lime content to a low lime content the red color of a stain is gradually destroyed.

By reducing the lime content in our enamel to below 0.2 equivalent and substituting some lead, zinc, and magnesium oxides, we obtained enamels which would burn to a good white color free from any pinkish tints.

Conclusions.—I do not wish to state that this is proof that there was a chrome tin compound formed in the enamel, as it hardly seems possible that, after several months of burning since the last of the terra cotta with the pink slip was finished, there would still be enough chromic acid present in the kilns to produce a perceptible pink color in the original enamel. However, the reduction in the lime content of our enamel was very effective in stopping the pink discoloration.

DISCUSSION WRITTEN AFTER READING THE PAPER.

Prof. Staley: In making cast iron enameled ware it is quite common to produce enamels with a slight pink blush. At one time this tint became so popular that some manufacturers, who could not produce it otherwise, added a small amount of MnO_2 to their enamel to produce the desired hint of a pink color. There is no probability of this tint being due to the presence of chromium, for chromium compounds are not used in cast iron enamels. The color is found in enamels high in calcium. It is especially pronounced when such enamels have been fritted and fused onto the iron under strongly oxidizing conditions.

I mention this as a phenomenon similar to, but not necessarily the same as, that described by Mr. Albery.

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SOME CHEMICAL REACTIONS OF INTEREST TO THE PLATE GLASS CHEMIST.

By F. GELSTHARP.

INTRODUCTION.

In making certain investigations relating to the making of plate glass, I have often been unable to find published information regarding the pyrochemical properties of some of the materials and the reactions which take place at the comparatively high temperatures we use in glass furnaces. We seem to have very much information available regarding the properties and reaction of common materials at ordinary temperatures and in solution; but the information of high temperature properties and reaction is not at all plentiful. There is no doubt that much is already known, but it has not been compiled in form for easy reference, so that in making investigations, if one has not the opportunity of searching the files of published matter efficiently, he must in many cases repeat what others have already determined. I am afraid I may be in this position and can only hope to be pardoned.

In this paper I do not presume to give very accurate scientific data, but rather the results so far obtained in a preliminary way, which however have enabled us to understand our own problems a little more clearly than heretofore.

STATEMENT OF THE PROBLEM.

The materials used in the manufacture of plate glass are sand (SiO_2), soda ash (Na_2CO_3), saltcake (Na_2SO_4), common salt (NaCl), limestone ($CaCO_3$), coal or charcoal (C), and white arsenic (As_2O_3). In order to become properly acquainted with the chemistry of glass-making we must know:

I. The degree of fineness and chemical composition or analysis of each material.

II. The pyrochemical properties of each material, including: (*a*) what is its melting point? (*b*) does it dissociate and at what temperature? (*c*) does it volatilize and at what temperature?

III. What reactions take place when any two or more of the

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materials are mixed at high temperatures? What are the properties of the compounds formed?

IV. Are any of the reactions incomplete, thus leaving some of the material in solution in the glass? Or is the excess volatilized?

V. What are the physical properties of the compounds (silicates) produced?

VI. How do the various silicates formed affect the viscosity and other physical properties of the resulting glass?

VII. What eutectics should, or do, we produce?

VIII. Is the sum of the heat effect of the reactions endothermic or exothermic?

IX. What are the properties of the possible impurities in the material, and their effect on the final reaction?

X. What are the properties of the materials and also of the ultimate glass in respect to the clay of the glass pots?

Of course, I do not propose to cover these queries as it is quite a field for investigation and we have, so far, touched only the outside of it.

TABULATION OF PUBLISHED DATA.

The following information regarding the pyrochemical properties of these materials has been obtained from published matter.

SINGLE CHEMICALS.

(1) Sand: Changes to tridymite at 800° C., melting point 1600° C. It combines with bases to form more or less fusible silicates.

(2) Soda Ash: Melts without decomposition at 850° C.; some dissociation at higher temperatures.

(3) Saltcake: Melts without decomposition at 863° C.; some dissociation or volatilization at higher temperatures.

(4) Common Salt: Melts without decomposition at 774° C. and volatilizes at 815° C.

(5) Limestone: Dissociates completely at 900° C., forming CaO.

(6) Coal or Charcoal: Active reducing agent.

(7) White Arsenic: Volatilizes without melting at 150 to 200° C.; may act as reducing or oxidizing agent according to conditions.

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MIXTURES OF TWO COMPONENTS.

(8) Sand + Soda Ash: React, forming silicate of soda. There seems to be no real limit to the increasing proportion of sand above monosilicate ($Na_2O\ SiO_2$). The viscosity increases and solubility in water decreases as SiO_2 increases. "Reaction appreciable at 700° C. and increased at 800° C. At 850° C. the Na_2CO_3 fuses and reaction is complete at 930° C. $Na_2O\ SiO_2$ is a mobile liquid at 1150° C. and is glass on cooling." (J. W. Cobb, Jour. Soc. Chem. Ind., XXIX, 399–404.)

(9) Sand + Saltcake: No information.

(10) Sand + Common Salt: In presence of water vapor, silicate of soda and HCl formed. No further information.

(11) Sand + Limestone: $CaO\ 2SiO_2$ and $CaO\ SiO_2$ are probably formed; the melting point of the eutectic between these two calcium silicates is 1410° C. According to proportions, other silicates may be formed with higher melting points.

(12) Sand + Coal or Charcoal: No reaction except at very high temperatures.

(13) Sand + White Arsenic: No information (nothing probable).

(14) Soda Ash + Saltcake: No reaction (G. Lunge).

(15) Soda Ash + Common Salt: No reaction (G. Lunge).

(16) Soda Ash + Limestone: Dissociation of limestone and fusion of soda ash, with some loss of Na_2O. (J. W. Cobb, Jour. Soc. Chem. Ind., XXIX, 799–802.)

(17) Soda Ash + Coal or Charcoal: Reduction of Na_2CO_3 at high temperatures with formation of sodium vapor.

(18) Soda Ash + White Arsenic: No information.

(19) Saltcake + Common Salt: No reaction (G. Lunge).

(20) Saltcake + Limestone: No reaction (G. Lunge).

(21) Saltcake + Coal or Charcoal: Reduction to sodium sulphides.

(22) Saltcake + White Arsenic: No information.

(23) Common Salt + Limestone: No reaction (G. Lunge).

(24) Common Salt + Coal or Charcoal: No information (nothing probable).

(25) Common Salt + White Arsenic: No information (nothing probable).

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(26) Limestone + Coal or Charcoal: Dissociation of limestone goes on more freely.

(27) Limestone + White Arsenic: No information.

(28) Coal or Charcoal + White Arsenic: Reduction to metallic arsenic which sublimes.

MIXTURE OF THREE COMPONENTS.

(29) Sand + Soda Ash + Saltcake: No further information than already stated for two components.

(30) Sand + Soda Ash + Common Salt: Ditto.

(31) Sand + Soda Ash + Limestone: Mixture of silicates formed, solubility, fusibility, and transparency, depending on proportions.

(32) Sand + Soda Ash + Charcoal: No further information than already stated for two components.

(33) Sand + Soda Ash + White Arsenic: Ditto.

(34) Sand + Saltcake + Common Salt: Ditto.

(35) Sand + Saltcake + Limestone: Ditto.

(36) Sand + Saltcake + Charcoal: Form silicate of soda when used in proper proportions (G. Lunge).

(37) Sand + Saltcake + Arsenic: No further information than already stated for two components.

(38) Sand + Common Salt + Limestone: Ditto.

(39) Sand + Common Salt + Charcoal: Ditto.

(40) Sand + Common Salt + White Arsenic: Ditto.

(41) Sand + Limestone + Charcoal: Ditto.

(42) Sand + Limestone + White Arsenic: Ditto.

(43) Sand + Charcoal + White Arsenic: Ditto.

(44) Sand + Soda Ash + Saltcake + Common Salt + Limestone + Charcoal + White Arsenic: When these are in proper proportions, several reactions take place with the result that a mixture of silicates of soda and lime are produced which is known as glass.

We might extend the series to other three-component and four-component mixtures, but there would be no advantage, since the foregoing cover all probable reactions. The above information is very meagre but is all I was able to learn from what literature I have consulted. I have, of course, omitted what is not of interest to the glass-maker.

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QUESTIONS FOR FURTHER STUDY.

In going over the above, I think we may omit from further consideration all except the following, which we will note as questions on which we require further information.

(3) Saltcake: The extent of dissociation at various temperatures?

(8) Sand + Soda Ash: Reactions most probable in glass melting?

(9) Sand + Saltcake: Possible reaction?

(10) Sand + Common Salt: Limits of reaction in glass melting?

(18) Soda Ash + White Arsenic: Possible reaction?

(20) Saltcake + Limestone: Possible reaction?

(22) Saltcake + White Arsenic: Possible reaction?

(27) Limestone + White Arsenic: Possible reaction?

(29) Sand + Soda Ash + Saltcake: Possible reaction of the saltcake?

(31) Sand + Soda Ash + Limestone: Limits for proportion of limestone?

(35) Sand + Saltcake + Limestone: Possible reaction of the saltcake?

(36) Sand + Saltcake + Charcoal: Possible reaction if sodium sulphides are also formed?

(43) Sand + Soda Ash + Saltcake + Common Salt + Limestone + Charcoal + White Arsenic (glass mixture): Combination of all possible reactions when perfectly and imperfectly mixed?

(44) Action of all the raw materials and also of glass produced on the clay of the containing pot?

EXPERIMENTAL WORK.

(3) **Saltcake: Dissociation or Volatilization Temperature.**—2.9262 grams of fused, C. P. Na_2SO_4 was placed in a small covered platinum crucible which was enclosed in a larger one. This was placed on calcined magnesia inside of a fire clay crucible in a small furnace. A pyrometer element was inserted inside the fire clay crucible so that the temperature could be regulated, and the furnace condition was kept strictly oxidizing. At intervals of one hour, the inner platinum crucible containing the

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weighed amount of Na_2SO_4 was withdrawn and weighed when cold.

There was no loss in weight until a temperature of 1310° C. was reached. The following results were obtained:

1310° C. Loss in wt. in 1 hour 0.0189 gr. = 0.646% of original Na_2SO_4 used
1370° C. Loss in wt. in 1 hour 0.0618 gr. = 2.110% of original Na_2SO_4 used
1430° C. Loss in wt. in 1 hour 0.1535 gr. = 5.250% of original Na_2SO_4 used
1490° C. Loss in wt. in 1 hour 0.3847 gr. = 13.100% of original Na_2SO_4 used

The resulting mass was tested for free alkali and found to contain 1.27 per cent. Na_2O. This was present as carbonate = 2.17 per cent. Na_2CO_3. A trace of platinum was also found in the melt. We, therefore, concluded that Na_2SO_4 begins to dissociate at about 1300° C. and the rate of dissociation increases rapidly with increase of temperature.

(8) **Sand + Soda Ash.**—Pure silica, ground to pass a 200 mesh sieve, was intimately mixed with anhydrous Na_2CO_3 and heated in a platinum crucible at a temperature of 131° C.

Experiment I. 1.06 grams Na_2CO_3 + 0.60 gram SiO_2, *i. e.*, 1 equivalent in centigrams of each, was used in order to form monosilicate of soda ($Na_2O\ SiO_2$). There was an energetic reaction, and when gas ceased to be liberated, a perfectly clear glass was produced. The loss in weight corresponded with the amount of CO_2 in the Na_2CO_3 used.

Experiment II. 1.06 grams Na_2CO_3 + 1.20 grams SiO_2, *i. e.*, 1 equivalent in centigrams Na_2CO_3 and 2 equivalents in centigrams SiO_2, was used in order to form bi-silicates of soda ($Na_2O\ 2SiO_2$). Gave result similar to Experiment I.

Experiment III. 1.06 grams Na_2CO_3 + 1.80 grams SiO_2, *i. e.*, 1 equivalent in centigrams Na_2CO_3 and 3 equivalents in centigrams SiO_2, was used in order to form tri-silicate of soda ($Na_2O\ 3SiO_2$). After the reaction was over, there was the same loss in weight as in Experiments I and II. But on examination the mass was found to contain a considerable amount of undissolved silica in suspension. This melt was returned to the furnace and the temperature continued about half an hour, when it was again examined and found to be perfectly clear glass, although no further reaction seemed to take place.

The conclusion I draw from these experiments is that in a mix-

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ture of soda ash + excess of sand, we may have formed $Na_2O\ SiO_2$ or $Na_2O\ 2SiO_2$ or mixture of these depending on the intimacy of the soda ash and sand mixture. The most predominating would be the bi-silicate, and by continued heating these silicates would dissolve the excess of sand, finally producing a homogeneous glass.

(9) **Sand + Saltcake.**—We used the same apparatus as for dissociation of Na_2SO_4. Pulverized, fused, C. P. Na_2SO_4 and pure silica, ground to pass a 200 mesh sieve, were taken in the proportions to form $Na_2O\ 4SiO_2$ and oxidizing conditions were maintained in the furnace. The mixture, freshly made up for each trial, used was 0.71 gram Na_2SO_4 + 1.20 grams SiO_2. It was heated at the following temperatures:

870° C. no loss		
925° C. for 30 min.	Loss in wt. = 0.0066 gr. SO_3 =	1.65% Na_2SO_4 reacted
980° C. for 30 min.	Loss in wt. = 0.0065 gr. SO_3 =	1.65% Na_2SO_4 reacted
1040° C. for 30 min.	Loss in wt. = 0.0100 gr. SO_3 =	2.50% Na_2SO_4 reacted
1090° C. for 30 min.	Loss in wt. = 0.0348 gr. SO_3 =	8.70% Na_2SO_4 reacted
1150° C. for 30 min.	Loss in wt. = 0.0693 gr. SO_3 =	17.30% Na_2SO_4 reacted
1200° C. for 30 min.	Loss in wt. = 0.1947 gr. SO_3 =	48.70% Na_2SO_4 reacted
1260° C. for 30 min.	Loss in wt. = 0.2612 gr. SO_3 =	65.30% Na_2SO_4 reacted
1310° C. for 30 min.	Loss in wt. = 0.3687 gr. SO_3 =	92.10% Na_2SO_4 reacted
1310° C. for 15 min.	Loss in wt. = 0.2598 gr. SO_3 =	64.70% Na_2SO_4 reacted
1310° C. for 45 min.	Loss in wt. = 0.3965 gr. SO_3 =	99.10% Na_2SO_4 reacted

A perfectly clear glass was produced in the last trial.

The conclusion I draw from this is that Na_2SO_4 reacts with SiO_2, beginning near the melting point of Na_2SO_4, and the rate or energy of the reaction depends on the temperature.

It may be of interest to give the results of another experiment in which the proportion of silica was very much less, *viz.*, in proportion to form $Na_2O\ SiO_2$. 2.13 grams Na_2SO_4 + 0.90 gram SiO_2 were taken and treated in the following way, only one sample being used:

1370° C. for 30 min.	Loss in wt. = 0.2583 gr. SO_3 =	21.5% Na_2SO_4 reacted and dissociated
1370° C. for 60 min.	Loss in wt. = 0.3805 gr. SO_3 =	31.7% Na_2SO_4 reacted and dissociated
1370° C. for 120 min.	Loss in wt. = 0.5195 gr. SO_3 =	43.3% Na_2SO_4 reacted and dissociated
1370° C. for 130 min.	Loss in wt. = 0.5921 gr. SO_3 =	49.3% Na_2SO_4 reacted and dissociated

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Another separate trial gave the following results:

1400° C. for 60 min. Loss in wt. = 0.5073 gr. SO_3 = 42.3% Na_2SO_4 reacted and dissociated

A complete reaction would have shown a loss of 1.20 grams. In this case, the reaction cannot complete itself; a clear glass is formed at the bottom of the crucible and is covered by a layer of Na_2SO_4. No free silica is left to react with the excess of Na_2SO_4. The gradual increase in the loss of weight after the first reaction is simply dissociation.

(10) **Sand + Common Salt.**—This experiment was conducted with the grade of materials used in glass-making, that is, sand passing a 40 mesh sieve but in large portion remaining on a 60 mesh, and salt of coarse grained quality and rather damp, containing 5 per cent. moisture. The proportions used were 120 of sand to 61.5 of salt, so if the whole of the NaCl reacted, we should produce $Na_2O\ 2SiO_2$. The materials were intimately mixed and placed in a fire clay crucible, the temperature of which was slowly raised to 1370° C. NaCl fumes passed off freely and the heat was continued till nothing condensed on a cold iron bar held over the crucible. On cooling, the mass was found to contain a large amount of soluble chloride. It was returned to the furnace and the temperature raised to 1400° C. for three hours. When cooled, it was now found to be free from soluble chloride, and the mass appeared as glazed sand grains loosely fritted together. This was analyzed and found to be composed of:

Na_2O	1.01%, equivalent to 1.906 NaCl.
SiO_2	98.99

Therefore, with the above conditions, it is possible for 1.92 grams of NaCl to react with 100 grams of SiO_2. This reaction cannot be anything more than a mere surface reaction in respect to the sand grains. Whether the reaction is according to only one or both of the following equations, I am not prepared to say.

$$2NaCl + 2SiO_2 + H_2O = Na_2O2SiO_2 + 2HCl$$
$$4NaCl + 5SiO_2 = 2(Na_2O2SiO_2) + SiCl_4$$

I believe the first is the more probable; and it is easy to conceive how, by reason of the presence of water vapor, the sand grains first become coated with a film of silicate of soda which prevents any further chance of the reaction continuing beyond this state.

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(18) **Soda Ash + White Arsenic.**—Not investigated.

(20) **Saltcake + Limestone.**—A mixture of 1 equivalent of $CaCO_3$ and 1 equivalent of Na_2SO_4 was heated in a platinum crucible to 1000° C. The Na_2SO_4 fused, and there was considerable evolution of CO_2 gas. The mass was ground up and digested with cold water repeatedly to remove soluble salts. The residue after filtering and washing was found to be a mixture of $CaCO_3$ and CaH_2O_2 but it was not free from sulphate, possibly due to imperfect washing. There is evidently no reaction between the Na_2SO_4 and $CaCO_3$.

(22) **Saltcake + White Arsenic.**—Not investigated.

(27) **Limestone + White Arsenic.**—Not investigated.

(29) **Sand + Soda Ash + Saltcake.**—With such a mixture, we know that a silicate of soda will be produced; but we wish to know how the physical properties of such a silicate compare with those of a silicate made from sand + soda ash alone, and what amount of Na_2SO_4 can be retained in solution in the silicate of soda produced. Not yet investigated.

(31) **Sand + Soda Ash + Limestone.**—This mixture forms silicate of soda and lime. In certain proportions it may form true glass. We wish to know what are the limits for the proportion of limestone and soda ash to produce permanent glasses. Not yet investigated.

(34) **Sand + Saltcake + Common Salt.**—These will produce silicate of soda by the reaction of $SiO_2 + Na_2SO_4$ and to a small extent by reaction of $SiO_2 + NaCl + H_2O$. But what we wish to know further is whether the NaCl may react in conjunction with the $SiO_2 + Na_2SO_4$ reaction thus:

$$Na_2SO_4 + 2NaCl + 4SiO_2 = 2Na_2O4SiO_2 + Cl_2 + SO_2$$

or

$$\begin{cases} Na_2SO_4 + 2SiO_2 & = Na_2O2SiO_2 + SO_3 \\ 2NaCl + SO_3 + 2SiO_2 & = Na_2O2SiO_2 + Cl_2 + SO_2. \end{cases}$$

We have not investigated this possibility.

(35) **Sand + Saltcake + Limestone.**—We have not made any experiments with such a mixture. With certain proportions a glass will be produced, and we wish to know what the limits of those proportions are.

(36) **Sand + Saltcake + Charcoal.**—When we have the right

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proportions of charcoal to saltcake, there is produced silicate of soda, thus (G. Lunge):

$$2Na_2SO_4 + C + 4SiO_2 = 2(Na_2O\ 2SiO_2) + 2SO_2 + CO_2.$$

But when the charcoal is in excess of this, there is also produced some sulphide of sodium, thus:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

This latter reaction is not so simple as stated, because instead of simply Na_2S we invariably have a polysulphide of sodium formed, which colors the silicate of soda a yellow or amber color. We might formulate an equation producing a polysulphide of sodium thus:

$$2Na_2SO_4 + 4C = Na_2CO_3 + Na_2S_2 + 2CO_2 + CO,$$

the Na_2CO_3 forming silicate of soda which dissolves the polysulphide. We have dissolved such a silicate of soda in hydrofluoric acid with the separation of free sulphur and evolution of sulphuretted hydrogen. This gives us confidence in the assertion that a polysulphide is formed.

(43) **Sand + Soda Ash + Saltcake + Common Salt + Limestone + Charcoal + White Arsenic.**—When in proper proportions and intimately mixed, a practically insoluble, homogeneous glass is produced. The reactions which take place are usually expressed as:

1. $Na_2CO_3 + nSiO_2 = Na_2O\ nSiO_2 + CO_2$.
2. $CaCO_3 + 2SiO_2 = CaO\ 2SiO_2 + CO_2$.
3. $2Na_2SO_4 + C + 2SiO_2 = 2(Na_2O\ 2SiO_2) + 2SO_2 + CO_2$.
4. $2NaCl + H_2O + SiO_2 = Na_2O\ SiO_2 + 2HCl$.
5. As_2O_3 oxidizes iron and volatilizes.

These serve to give a general idea. But in the making of glass there are many phenomena which the above equations fail to explain. The reactions are evidently very much more complicated.

We have present all the materials used in the old Le Blanc soda process which produced a waste material, calcium sulphide, in addition to soda ash, thus:

$$Na_2SO_4 + CaCO_3 + C = Na_2CO_3 + CaS + CO_2 \text{ (G. Lunge)}$$

This reaction will take place below 1000° C. The extent to which it can take place in a glass mixture will be modified by the presence of SiO_2, but it is sure to take place to some extent. Here

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we would have a new material (CaS) introduced, which further complicates the reactions.

We have shown that we may have unconsciously introduced in the melt Na_2S, or Na_2S_2, and CaS. Recently, attention has been called to the reaction of metallic sulphides on $CaSO_4$ and $BaSO_4$ (W. Schutz, Metallurgie, VIII, 228–46; and H. O. Hofman and W. Mostowitsch, Bull. Am. Inst. Min. Eng., XLVII, 917–39), and we have found that similar reaction takes place with Na_2SO_4 under certain conditions. I intend to cover this inquiry regarding action of sulphides on Na_2SO_4 in the near future. There is also the effect of certain impurities in the materials to be considered such as $CaSO_4$, Fe_2O_3, and Al_2O_3. These, however, are not present to any large extent.

Reactions of $CaSO_4$.—Dissociation of $CaSO_4$. H. O. Hofman and W. Mostowitsch (Chem. Eng., IX, 152–4) determined that dissociation takes place at 1200° C. and is complete at 1360° C., and found that SiO_2 lowers the temperature of complete decomposition. We found that 1.36 grams of $CaSO_4$ held at a temperature of 1370° C. for one hour lost 0.4451 gram SO_3, equal to a percentage loss of 32.7. This is equivalent to 55.6 per cent. of the $CaSO_4$ dissociated in one hour.

$CaSO_4$ + SiO_2.—C. P. $CaSO_4$ and purified sand, ground to pass a 200 mesh sieve, were used. 0.68 gram $CaSO_4$ and 1.20 grams SiO_2 (*i. e.*, 1 equivalent of $CaSO_4$ to 2 equivalents of SiO_2) were taken, intimately mixed, and heated in a platinum crucible in an oxidizing atmosphere with the following results:

1090° C. for 30 min. Loss in wt. = 0.1023 gr. SO_3 = 25.57% of $CaSO_4$ reacted
1200° C. for 30 min. Loss in wt. = 0.2852 gr. SO_3 = 71.30% of $CaSO_4$ reacted

Total loss in wt. = 0.3875 gr. SO_3 = 96.87% of $CaSO_4$ reacted

0.4 gram loss would represent a complete reaction. This reaction evidently takes place at about twice the rate of its sister reaction with saltcake (Na_2SO_4), and we would, therefore, expect it to take place prior to it where both materials were present.

$CaSO_4$ + C.—H. O. Hofman and W. Mostowitsch (Bull. Am. Inst. Min. Eng., XLVII, 917–39) give the following reaction:

1. $CaSO_4 + 4C = CaS + 4CO$.
2. $CaSO_4 + 4CO = CaS + 4CO_2$.
3. $3CaSO_4 + CaS = 4CaO + 4SO_2$.

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The first reaction commences at 700° and is complete at 1000° C. Below 800° C., CO_2 is formed; but above 800° C., CO is formed. Therefore, CO reduces $CaSO_4$ more readily than C. The second reaction commences at 680° C. and is complete at 800° C. The third reaction begins at 800° C. and is energetic between 850° and 900° C.

$CaSO_4$ + Glass.—We have found that when $CaSO_4$ is mixed with ground glass and held at a temperature of 1370° C. (that is, at the firing temperature of glass) for a sufficient length of time, the CaO of the $CaSO_4$ is taken up by the glass and $NaSO_4$ separates out on the surface. The Na_2SO_4 later entirely disappears by dissociating, the Na_2O being partly volatilized and partly taken up again by the glass. This requires further investigation, which we hope to give it.

It has been stated by some writers on plate glass manufacture that the Na_2SO_4 used in a glass batch is reduced to Na_2SO_3 by C. This we conclude is very improbable if not impossible. All our attempts to produce Na_2SO_3 by reduction of Na_2SO_4 by C were futile. But considering that there might possibly be some peculiar conditions in glass melting which allowed Na_2SO_3 to be produced, we carried the investigation further. C. P. Na_2SO_3 was procured and heated in a closed crucible to fusion. The Na_2SO_3 was completely decomposed, producing a mixture of Na_2SO_4 and Na_2S. The probable change was:

$$4Na_2SO_3 = 3Na_2SO_4 + Na_2S$$

C. P. Na_2SO_3 was then heated to fusion in an atmosphere of SO_2. The Na_2SO_3 was entirely converted into Na_2SO_4 with liberation of sulphur. It, therefore, does not seem possible that Na_2SO_3 could be produced in melting glass batch.

I regret that this paper is very incomplete, but I hope to be able to continue these investigations and to give the results at some future time.

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Dr. Tillotson: Mr. Gelstharp is to be commended for the very systematic outline of his proposed research. Two thoughts come to me on reading it over. (1) In a systematic study of all possible reactions, new facts of utmost importance and value

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are always to be found, often in the most unexpected places. (2) Reactions in a simple system may not take place in a more complex system.

Mr. Gelstharp has selected for study about fourteen reactions out of a possible forty-four. He doubtless intended that these fourteen are to be studied first, reserving the other for a later period. The results obtained in the reaction between saltcake and sand are very interesting. In the experiment in which 2.13 grams Na_2SO_4 and 0.90 gram SiO_2 were taken, the reaction was not complete and a layer of Na_2SO_4 over a layer of glass was produced. From the proportions taken and the amount of loss, it appears that this glass possessed the composition $Na_2O\ 2SiO_2$. It would be interesting to know if Na_2SO_4 could be made to react with $Na_2O\ 2SiO_2$, $Na_2O\ 3SiO_2$, etc., both, of course, being intimately mixed. This seems to be a reaction which may throw some light upon the chemical compounds which soda and silica may form in a glass.

The behavior of Na_2SO_3 at high temperatures is rather unexpected. But this, I think, does not disprove the possibility that Na_2SO_4 may be reduced to Na_2SO_3 by carbon. In the melting process we have a complex system and the resulting products will depend in no small degree on the velocity of the reactions. Thus if the reaction $4Na_2SO_3 = 3Na_2SO_4 + Na_2S$ is very rapid we would not expect to find any sodium sulphite on heating saltcake with carbon, even if it were formed. But if $Na_2SO_3 + SiO_2 = Na_2SiO_3 + SO_2$ were a rapid reaction the production of SO_2 when saltcake, carbon and sand are melted together is explained. If Na_2SO_3 is not formed, I do not understand why SO_2 should be liberated during the fusion process.

This and other similar questions may be answered only by the accumulation and correlation of a large amount of data.

Mr. Gelstharp: Dr. Tillotson gives us the suggestion that $Na_2O\ 2SiO_2$ was probably formed in our experiment with 2.13 grams of Na_2SO_4 and 0.90 gram SiO_2. The result would indicate this. In making a repetition of this experiment I would try to prove if this were so.

It certainly would be of value to know whether Na_2SO_4 will react with $Na_2O\ SiO_2$, $Na_2O\ 3SiO_2$, etc. This will be investigated as the opportunity presents itself.

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BEHAVIOR OF AN ACID GLASS IN A TANK FURNACE.

By J. M. KNOTE, Pittsburgh, Pa.

It is no ordinary thing for a glass manufacturer to be troubled by devitrification of the ware at the furnace. In the case described below, the trouble took the form of white streaks through the machine-made bottles. It developed on investigation that the white tail or streaks represented the glass left sticking to the dipping rod after the piece of viscous glass had been cut off for the formation of the previous bottle. On putting the rod back into the furnace, this remnant blended imperfectly with the new lump of glass and a white steak resulted in the next bottle.

The factory worked two tank furnaces, one delivering eight tons per day and the second twelve tons. The gas supply was equally divided between the two. No trouble of the kind mentioned was experienced on the small furnace but all on the large one and most severely on the machines making large bottles. It also developed that the trouble grew better or worse as the gas pressure was high or low. A sample of glass was taken from each tank while the smaller one was delivering good ware and the larger one causing much trouble. The analyses are as follows:

		Small tank	Large tank		
Glass I	Silica	77.0%	77.3%	Empirical formula	
	Lime	4.62%	4.52%	Magnesia 0.2	Silica 3.13
	Magnesia	3.26%	3.24%	Lime 0.2	
	Soda	15.1%	15.94%	Soda 0.6	

It was thought at first that the mixer had accidentally changed his formula or the raw materials had changed, but glass from a bottle three years old analyzed as follows:

Glass II	Silica	76.45%
	Lime	4.05%
	Magnesia	2.8 %
	Soda	16.7 %

So it is evident that no appreciable change had occurred, and this formula had been in use for years. In contrast to this formula a factory near by was making a glass:

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Glass III	Silica	73.10%
	Lime	13.47%
	Magnesia	0.5 %
	Soda	12.1 %

The chief points of interest in this case are how much the composition of the glass made in some places varies from the most desirable composition, the effect of high silica on glass in actual practice, and the influence of temperature and method of working on glassware.

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Dr. Tillotson: Mr. Knote's paper offers some very good problems in the physical chemistry of silicates, and I am sorry that he did not present a more lengthy discussion of his observations.

In the first place, the question of devitrification is all important in the production of perfect glassware. We know that devitrification is caused by the crystallization and segregation of some component or components of the glass, and we know that devitrification may be induced in many glasses by subjecting them to a temperature either at or just below that at which the glass begins to soften. Tammen in his book "Krystallisieren und Schmelzen" has set forth[1] mutual relationship between the viscosity, melting point, velocity of crystallization and tendency to spontaneous crystallization, and has shown that the velocity of crystallization has a maximum value at a temperature just below the "melting point." The same phenomena are observed[2] in the manufacture of gold ruby glass.

The data given by these observers explain the facts that a glass may be rapidly cooled from a high temperature to one below its melting point without visible devitrification taking place. Crystalline nuclei are, however, always formed, and if the glass is reheated to the softening point, they may serve as seeds for larger crystals, resulting in devitrification of the glass; so it is not surprising that the glass left on the dipping rod should devitrify on being again introduced into the furnace, for while the glass in the tank, on account of its high viscosity, may not de-

[1] See also Bleininger, these Transactions, IX, 427, 1907.

[2] Zsigmondy, "Colloids and the Ultramicroscope, p. 165, et seq.

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vitrify, although it is in a supercooled condition and needs only the presence of nuclei to start the growth of crystals, yet the crystals in the glass on the dipping rod will not disappear unless subjected to a temperature considerably above the gathering temperature.

Another point must not be overlooked, and that is the temperature at which the change is melted. This is an important factor because it not only controls the completeness of the chemical reaction and of the chemical equilibrium, but also because it controls the degree of physical homogeneity in the glass. A higher temperature produces a more fluid melt in which chemical equilibria and physical homogeneity are more readily attained. Mr. Knote observed that a higher gas pressure, which presumably gave a higher temperature, produced a more workable glass, and that glass from the small furnace gave little trouble. This is doubtless due to the higher temperature attained during the actual melting and fining of the glass in the small furnace.

In his closing paragraph, Mr. Knote is disappointingly brief. We should have liked to know his ideas on "the most desirable composition" and on "the effect of high silica on glass in actual practice."

In this connection, I should like to suggest a method for expressing the composition of a glass which shows at a glance a little more than the empirical formula as given by Mr. Knote. If we denote the alkaline earth oxides by RO and the oxides of the alkalies by R_2O, Glasses I and III may be expressed as follows:

I. $(RO.SiO_2) + 1.49\ (R_2O.4.55SiO_2)$.

III. $(RO.SiO_2) + 0.77\ (R_2O.\ 5.36SiO_2)$.

The assumption that the alkaline earths exist as metasilicates in the glass is partially justified from the fact that only metasilicates of calcium and magnesium have been observed in devitrified glasses, but the more important part of the system is in the ratios 1.49 and 0.77 which represent $\frac{\text{equiv. } R_2O}{\text{equiv. } RO}$ which is a most important ratio in determining many of the physical properties of a glass but more especially that of devitrification. The ratios 4.55 and 5.36 are indices of the "acidity" of the glass and

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show, in this case, that a glass with a lower per cent. of SiO_2 may be a more "acid" glass.

Mr. Gelstharp: I happen to be acquainted with the case cited in this paper, having inspected some of the defective bottles and samples of the glass batch used in the tanks. I would ascribe the cause of the trouble to "devitrification" (agreeing with Mr. Knote).

Such glass described as Glass I, analysis of which is given, would be very much inclined to devitrify or crystallize. The glass-maker should know that when his source of alkali is soda ash alone, there is a fixed minimum limit for the ratio of soda to lime and magnesia, beyond which he cannot go without risk of getting into trouble in the nature of white scum or by producing a glass which easily devitrifies. The limit appears to be near 2 to 1, that is:

$$Na_2O : CaO + MgO :: 2 : 1.$$

In such a desirable glass the molecular empirical formula would be:

$$\left.\begin{matrix} CaO \\ MgO \end{matrix}\right\} 0.33 \Bigg\} SiO_2\ x$$
$$Na_2O\ 0.66 \Big\}$$

Now Glass I is given in the paper as:

$$\left.\begin{matrix} CaO & 0.2 \\ MgO & 0.2 \\ Na_2O & 0.6 \end{matrix}\right\} SiO_2\ 3.13$$

The ratio here is:

$$Na_2O : CaO + MgO :: 1.5 : 1.$$

This glass under favorable conditions devitrifies.

Glass II made three years ago is represented by:

$$\left.\begin{matrix} CaO & 0.175 \\ MgO & 0.170 \\ Na_2O & 0.655 \end{matrix}\right\} SiO_2\ 3.1$$

The ratio in this case is:

$$Na_2O : CaO + MgO :: 1.95 : 1.$$

This glass does not devitrify and closely agrees with the desired ratio of 2 : 1.

The glass-maker should know this in order to compound his batch properly, but even this knowledge is not alone sufficient. He must have his materials analyzed and especially if he uses

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ground burnt lime instead of limestone, and still more important is this if the lime be dolomitic. Otherwise he is liable to get into much trouble.

I understand that the bottle machine referred to works out of the large tank only, that the glass left attached to the gathering rod is a condition which must be tolerated, and that the small tank is run on hand work, in which case the above mentioned condition does not exist. The reheating of the attached piece of glass assists crystallization or devitrification of such imperfect glass, while with a better proportioned glass the worst defect that would be produced would be a cord.

It is stated that the trouble is better or worse as the gas pressure is high or low. This may be due, to some extent, to a loss in the soda content making the ratio somewhat less; or if the working end of the tank is run hotter, the attached piece of glass may be raised in temperature past the critical stage of crystallization. In Glass I, we are right on the extreme limit and the smallest change is liable to affect it.

Glass III, which is referred to, could not be a glass made from soda ash alone as the source of alkali. This batch must contain saltcake, since it is impossible to make glass of so high a lime content without the use of some saltcake. This is a good type of glass and will not devitrify under ordinary conditions.

Mr. Knote makes the point that this devitrification trouble is the effect of high silica content and the influence of temperature. I do not think that in this case the high silica content is directly the cause of the trouble, but rather the ratio of the bases.

Mr. Frink: Mr. Knote's rather too brief paper on the subject of devitrification is of more than passing interest to the glass-maker. The subject is one which deserves very careful study and close application and exhaustive investigation whenever the opportunity presents itself, and usually this is not infrequent in a practical operating plant.

Using the term of "devitrification" as a general classification of all forms of crystallization which occurs in the manufacture of glass is sufficient for the glass-maker; however, in my opinion, this should be subclassed by differentiating between what I would call a true devitrification, that is, the crystallizing of the

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whole body of the metal, and the separating out, from a magma of glass, of crystals of those minerals or materials which are present in excess, or those which are more readily crystallized whenever certain temperature or pressure conditions happen to prevail.

Mr. Knote has cited two cases wherein he has shown quite clearly that it is largely a matter of temperature and pressure conditions that has caused his crystal forms, although, without doubt, the primary cause has been due to there being present an excess of one of the constituents, which in this case was silica.

By the aid of a petrographic microscope and the application of simple methods of optical mineralogy, it is quite easy to differentiate between crystals of silicates of the alkalies and alkali-earth metals and those of uncombined alkali-earth metals, the silicates of either of them, or free silica. The crystals which are the combined silicates of lime and soda or lime and potash are isometric, and, therefore, show substantially no extinction when the crystal is rotated between crossed nicols, while those of the soda silicate or lime silicate show extinction and, in the majority of cases, definite orientation, and quite often interference figures.

It would have been very interesting indeed to have subjected Mr. Knote's specimen to a microscopic analysis in conjunction with his chemical analysis. One of my methods is to take small portions of the glass containing the devitrified glass, or crystal substance, and free it as far as possible from the clear glass, and, by crushing in an agate mortar so that it will pass a 60- or 80-mesh sieve, examine a small portion in the microscope. I apply the powdered specimen to a microscope slide, immersing same in a mixture of oil of sassafras and oil of juniper (about 6 parts of sassafras to 4 parts of juniper). This mixture gives a refractive index of about 1.523 for sodium light, which is substantially the same as that of glass whose composition is approximately:

72.0%	SiO_2
13.5	Na_2O
12.5	CaO
0.5	MgO
1.5	Al_2O_3

A specimen thus prepared, when viewed between crossed nicols

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and with divergent light, of any magnification up to 800 diam., will reveal very little of the glass, or at least only faintly show the outlines of the glass particles, while crystals, of whatever form of character, unless perchance they should be of the same refractive index as the oil mixture, will show up very plainly and with good definition. Thus the extinction angle can be obtained, and also many of the other optical properties of the crystal can be studied, unless such crystals should be composed of the same materials as the glass itself and should be substantially free from stress.

In reviewing Mr. Knote's paper, I am of the opinion that this is an instance wherein silica was crystallized out, inasmuch as there appears to be a poor balance of the molecular equivalents. I believe that the glass of which Mr. Knote gives an analysis contains altogether too much silica and is too high in soda. It would appear quite certain that unless high temperatures were maintained a crystallization must inevitably take place, as I consider it quite necessary to maintain the molecular ratios such as approximate the chemical analysis given above. Our practice approaches this. Taking an analysis of recent date, it fairly well approaches what I term a normal glass, in which the silica equivalent equals 3 of silica to 1 of soda, and 3 of silica to 1 of lime. This analysis is as follows:

SiO_2	71.67
Na_2O	13.40
MgO	0.40
CaO	12.05
Al_2O_3	2.40
Fe_2O_3	0.08

Extending this in its approximate molecular proportions, it will be seen that the silica component would be 4,315, that of soda 831, lime and magnesia 692, alumina 204, and iron 12. Now let us consider that the alumina acts both as an acid and a base, and it may, therefore, be neglected in the consideration of the chemical equivalent ratio. As we now assume 3 molecules of silica to react with 1 of lime, and the same amount with 1 of soda, it will be seen that our glass will very closely conform to that of a normal or perfect glass, as we would have one-half

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of the molecular equivalent of SiO_2 (4,315) or 2,157.5 going to the soda, which, it will be seen, is substantially three times the soda molecular weight, which is 2,493, and likewise with the lime, which is 2,076. However, it will be seen that in order to have made this glass perfect, it would have been necessary to reduce the soda somewhat.

The adding of magnesia for the purpose of making the glass thinner, or, as is advisable to do in certain mechanical operations, to obtain a greater liquidity, or the adding of baryta to increase its brilliancy or for other purposes, does not alter the molecular ratios. At least my experience has been that in our practice, as is necessitated by present furnace construction and fuel application, the closer one can keep to the above mentioned ratios the less the breakage and the easier the handling obtained, and the fewer the imperfections to be contended with.

The factor of temperature is a very important one, but what is nearly as important is the factor of combustion or, in other words, the completeness and uniformity of combustion. Without doubt the products of combustion play a very important part in the maintaining of glass in a desirable condition, and, in my opinion, this is one of the factors which has caused one tank to show crystallization where another has been substantially free from it, even though the temperatures were the same.

Another factor which to a considerable extent governs crystallization is the velocity of movement of the glass while in the molten condition. By this I mean that a large tank from which but little glass is being taken is much more susceptible to crystallization at a given temperature than would be a smaller furnace from which the glass was being taken up to, or approaching, its capacity. This accounts for the finding of spherulites and other crystalline forms in "dead" corners, floater notches, or after a tank or pot has been blocked for a considerable period.

Fig. 1 shows the beginning of a crystallization. To the unaided eye these crystals were hardly discernible, but by slight etching with hydrofluoric acid they were brought out so that they were very prominent under the microscope, magnified about 80 diameters. They were due to the blocking of the tank for a considerable period of time.

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Fig. 1.—Crystals, caused by prolonged heating, just forming.

This glass was a trifle high in soda, and high in silica, or perhaps it would be more proper to state that it was low in lime. Quite likely the crystals observed by Mr. Knote were very similar to those shown in this figure.

Fig. 2 shows crystals where an excess of lime prevailed, that is, silica was about 68, soda 13, and lime 13.5 to 14, which composition produced a condition that caused a very hard working glass and one which was very difficult to melt. These crystals seemed to pervade the whole mass of glass, and although

Fig. 2.—Crystalline condition due to excess of lime.

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without microscopic examination there appeared to be no definite forms, the glass had a peculiar, slight opalescent appearance, which on etching clearly revealed these figures. Microscopic examination showed them to be a definite crystalline form, aggregated in the manner shown, their optical properties denoting them to be various compounds of lime and silica.

As to the variations and composition of glasses made in various places, I would say that in the analyses of something over a thousand different glasses, there are rarely any two, even for the same purpose, which agree in composition. The effect of high silica upon glass in actual practice, in my opinion, is very detrimental, and the cause of a great deal of trouble, unless one is working a furnace up to its capacity at all times, and unless he has more than ordinarily satisfactory means for controlling the temperature and the combustion.

Personally I am a great advocate of alumina, and I believe that when alumina is applied in the proper manner it assists in absorbing excess of either silica and soda, which, without the presence of alumina, would have a tendency to exist in an uncombined condition, making it imperative that the furnace conditions should be maintained more nearly uniform and to a given point. What constitutes that uniformity, or just what that point is, I doubt if there are any as yet able to specifically state.

It would be very interesting, and of great practical value, if more of such problems as Mr. Knote has called attention to would come before the Society.

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SOLUBILITY OF SOME SALTS IN GLASS.

By F. GELSTHARP.

INTRODUCTION.

Object of the Investigation.—We have made some careful chemical analysis of plate glass, made from the following materials: SiO_2, Na_2CO_3, Na_2SO_4, NaCl, $CaCO_3$, C, and As_2O_3. This work was done in order to determine whether the Na_2SO_4 and NaCl were entirely decomposed during the melting, or partly volatilized, or partly retained in the glass as Na_2SO_4 and NaCl.

Our knowledge of the deportment of these two salts leads us to believe that the following reactions may take place under condition of a glass melt:

$$2Na_2SO_4 + 4SiO_2 + C = 2(Na_2O\ 2SiO_2) + CO_2 + 2SO_2.$$

$$2Na_2SO_4 + 4SiO_2 = 2(Na_2O\ 2SiO_2) + 2SO_2 + O_2$$

or we may have simple dissociation at the fining temperature,

$$2NaSO_4 = 2Na_2O + 2SO_2 + O_2,$$

in the latter case some of the alkali being taken up by the glass and some volatilized. The NaCl may be decomposed to some extent according to the following reaction:

$$2NaCl + 2SiO_2 + H_2O = Na_2O\ 2SiO_2 + 2HCl.$$

Other possible reactions we have not established. If the NaCl is not all used up in this reaction, we would expect the remainder to be volatilized since the fining temperature of glass is about 530° C. above the volatilizing temperature of NaCl.

ANALYTICAL RESULTS.

Na_2SO_4.—According to the foregoing we should not expect to find either Na_2SO_4 or NaCl in the finished glass. But in our investigations, we find by chemical analysis considerable amounts of both these salts, although a microscopic examination fails to show their presence. No difference can be detected in the appearance of glass containing the salts when compared with glass that does not contain them.

The following are the amounts of Na_2SO_4 found in several samples of plate glass, made at various times and perhaps under slightly different conditions:

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Sample 1.	Per cent. of Na_2SO_4 found	0.59
2.	" " "	0.64
3.	" " "	0.65
4.	" " "	0.68
5.	" " "	0.74
6.	" " "	0.80
7.	" " "	0.85
8.	" " "	0.90
9.	" " "	1.01
10.	" " "	1.09
11.	" " "	1.11
12.	" " "	1.20
13.	" " "	1.21
14.	" " "	1.30
15.	" " "	1.74

We do not lose sight of the fact that some Na_2SO_4 may be found in glass made from materials which did not originally contain it. In such cases, the SO_3 is supposed to be absorbed during the melting from the furnace gases; but this did not amount to more than 0.22 per cent. of Na_2SO_4 in experiments we have made under the same conditions. So we feel justified in concluding that the Na_2SO_4 we find is from the original Na_2SO_4 used in the glass batch.

NaCl.—Of NaCl we found in samples of glass:

Sample 1.	Per cent. of NaCl found	0.91
2.	" " "	0.98
3.	" " "	1.48

Na_2SO_4 + NaCl.—In samples tested for both Na_2SO_4 and NaCl we found:

Sample 1.	Per cent. of	Na_2SO_4	found	0.85
	"	NaCl	"	0.91
2.	"	Na_2SO_4	"	0.64
	"	NaCl	"	1.48

From these results, we conclude that under ordinary conditions, it is possible to have about 1.0 per cent. of Na_2SO_4 and, if common salt is used in the batch, also 1.0 per cent. NaCl in solution in the residual glass.

We have found that by increase of temperature or increase of time at the same temperature the amount of Na_2SO_4 is decreased. As an example, glass was prepared and found to con-

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tain 0.90 per cent. Na_2SO_4. This was remelted and held at a temperature 50° C. higher than before for one hour with the result that the glass now contained only 0.65 per cent. Na_2SO_4. This was not tested for NaCl, but in making experiments we found that glass containing much NaCl continues to give off NaCl fumes.

An attempt was made to determine the maximum amount of Na_2SO_4 and NaCl plate glass could retain, but this depends so much on time of exposure to certain temperatures, that we considered it, for our purpose, necessary to consider only the ordinary plate glass fining temperature. The result, therefore, can apply to our special case only. But I believe they may be taken as approximately the maximum amounts that can remain in plate glass.

For Na_2SO_4 we found 1.74% maximum.
NaCl we found 1.48% maximum.

A very important fact regarding the water solubility of plate glass containing Na_2SO_4 and NaCl is that it is less soluble than that which does not contain these salts.

Fluorides and Sulphides.—There are two other interesting cases of solubility of salts in glass which might be mentioned here. One is the solubility of fluorides in opal glass, which is a very variable quantity. The depth of color largely depends on this. During the melting and fining, fumes of fluorides are given off freely, and long continued heat or increase of temperature will drive out almost the whole of the dissolved fluoride. Then there is the case of sulphides; very large amounts of CaS or Na_2S may be retained by glass. As to whether this is a case of solubility, or simple mixture, or actual chemical combination, we do not wish to commit ourselves.

Method of Analysis.—The methods of analysis used to determine the Na_2SO_4 and NaCl are those commonly known to all chemists. We omit particulars of individual experiments made, as they are unnecessary to the value of this paper.

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Dr. Tillotson: Mr. Gelstharp presents some interesting and important analyses, and it is to be hoped that the investigation

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will be continued. His observation that glasses containing a small amount of Na_2SO_4 and NaCl are less soluble than glasses which do not contain these salts brings to mind that the new Jena glassware, which is said to be annealed in gases containing SO_2, is much more resistant to water than glass annealed in the ordinary manner. The importance therefore of studying the effect of small amounts of what might be considered "impurities" in a glass is not to be overestimated.

Mr. Frink: I am much interested in Mr. Gelstharp's paper on "Solubility of Some Salts in Glass," because it shows an interest in, and is attacking a problem, the complete solution of which I believe would be of great interest and assistance to the glass-maker. While it differs considerably from the views which I have formerly held in the matter, the facts noted are, nevertheless, sufficient to prove that hurried or superficial observations, as were some of those on which I have based my opinions, are of more danger than of value, inasmuch as I have made several attempts to determine apparently unaccountable causes for certain effects and defects noted in the manufacture of window glass by machine process, which may be directly attributable to the presence of dissolved salts or small quantities of undecomposed salts, whether they be free or dissolved.

Mr. Gelstharp's statement as to the rather erratic manner in which sulphates may be present agrees perfectly with my own experience, and accounts for my opinions given some time ago of the improbability of there being present, even in minute traces, any SO_3 in the finished glass, and that it is quite improbable that there was sufficient quantity of this existing in the combined state with either soda or lime to be effective.

I, however, can not quite agree with Mr. Gelstharp's statement that that glass which contains any considerable quantity, say 0.5 per cent. or more, of Na_2SO_4 could be less soluble than that which contained no Na_2SO_4.

It would further be interesting to know under what conditions the glasses were made from which the samples 1 to 15 were taken, that is, were the melts made in open pots as in the melting of plate glass, the fire used being producer gas or natural gas, or were they made in covered pots or tank furnace, under prac-

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tical conditions or in laboratory experiments. In the tank there would be exceptional good opportunity for variations in the quantities of sulphates found. It would seem to me that a quantity of 1.74 per cent. of Na_2SO_4 would be markedly manifest in the properties of the glass and its solubility.

In the event that the analyses cited by Mr. Gelstharp in Nos. 1 to 15 were made of samples produced under conditions of melting whereby the fire came in direct contact with the major portion of the batch materials, such analyses would afford us a very good check upon furnace conditions, particularly the relation of combustion and degree of melting. If the analyses given are from substantially the same furnace conditions and batch formula, it would seem to be directly due to the reducing or specific action of the fire. It is well known among glass-makers that the amount to which "salt water" exists on the surface of the glass can be easily controlled by "producing a reducing heat" or, in other words, bring about a reducing action of the fire. While this is the prevalent method of accomplishing this result, a much better method is to always maintain the furnace under proper operating conditions so as to prevent the accumulation of "salt water," and obviate the necessity of such a step. The practice of producing reducing conditions for the purpose of volatilizing sulphur often involves the glass-maker in trouble due to the drop in temperature occasioned by the incomplete combustion and also causes cordy glass due to an entrainment of carbon in the event that he oversteps the line of safety when he reduces the air sufficient to obtain this result.

Again I would say that if it is possible to obtain methods for determining sulphates that may be readily applied in technical analyses without introducing errors to such an extent as to make such sulphate determinations worthless as a factor of control, it would without question make an admirable check upon furnace conditions. This is something which up to date I have not found, it being a well known fact that after the glass is once finished or taken from the furnace, there is nothing in the glass itself which may be used for determining whether or not it has been mixed and melted under proper conditions.

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Mr. Gelstharp: Regarding the water solubility of glass containing Na_2SO_4 and NaCl, one naturally would expect the glass to be more soluble, but all experiments I have made prove the contrary. In fact the solubility appears to simply depend on the percentage of alkali silicate contained in the glass. When we have present a greater amount of Na_2SO_4 and NaCl, the percentage of Na_2O is correspondingly less, and in such cases we always find the solubility to be less.

The glass was in every case melted in open pots using natural gas, but the batch weights were varied or the glass melted at varying temperatures. The amount of 1.74 per cent. Na_2SO_4 is the maximum amount I could produce in apparently good plate glass; this should not be considered as anything like a normal amount.

As to an analysis of the glass being a check on the melting conditions, it may be possible; but I am afraid it would not be very practical, unless batch weights were kept strictly correct and the mixture perfectly uniform. These two latter conditions I have found are very hard to maintain. Otherwise, I believe, Mr. Frink has made a very wise suggestion which might prove very practical in some glass works.

The following is an outline of one method of analysis I use for determination of SO_3 in glass:

Fuse 1 to 2 grams of finely ground sample with Na_2CO_3 in platinum crucible over alcohol blast lamp. Digest with water till completely disintegrated and make slightly acid with HCl. Boil well; add small quantity of paper pulp. Filter off SiO_2, using filter pump. Add to boiling solution just sufficient $BaCl_2$, boil for some time. Filter off $BaSO_4$, which contains some SiO_2. Burn filter paper at a low temperature. Treat residue in platinum crucible with HF and add a few drops of H_2SO_4. Heat to drive off SiF_4 and excess H_2SO_4. Fuse residue with Na_2CO_3. Take up with water; add a drop of HCl in excess to make acid and boil for some time. Filter and weigh the $BaSO_4$ remaining. From weight of $BaSO_4$ calculate SO_3 or Na_2SO_4.

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MATTE GLAZES.[1]

By Ross C. Purdy.

INTRODUCTION.

We have had considerable discussion, in our Transactions, of this type of glaze in which formulae of the glazes and theories on the cause of matteness have been given. Notwithstanding the seemingly exhaustive treatment which this subject has been given in the past, we found it very difficult to plan series exploiting the range in composition within which matte effects could be produced without resorting to the use of a tried formula as a base and then blindly making variations in the several glaze constituents. After collecting data from the reports of four different senior classes at the Ohio State University, we concluded that none of the theories so far advanced were wholly tenable or at least none of them gave a working hypothesis. With the work of each succeeding class, we gained new ideas, all of which pointed in one general direction; but it was not until this winter that these ideas finally resolved themselves into a theory that gives an absolutely reliable working hypothesis.

TWO TYPES OF LOW AND MEDIUM FIRE MATTE GLAZES.

There are two[2] general types of low and medium fire matte glazes:

I. Glazes of the ordinary raw lead type using from 0.5 to 0.7 equivalent PbO.

II. Glazes in which 0.2 to 0.4 equivalent of the lead has been replaced by BaO.

TYPE I. RAW LEAD MATTES.

A study of the work done on this type of matte glaze reveals the following conditions as being necessary to the development of a matte texture.

(*a*) There must be a certain ratio between the CaO from whiting and the Al_2O_3 from clay, this ratio being dependent upon the equivalent of feldspar used. The higher the feldspar equiva-

[1] Contribution from the Ceramic Engineering Laboratories of the Ohio State University.

[2] True crystalline matte glazes, such as the Teco, are not here considered.

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lent the lower must be the ratio of CaO to the Al_2O_3 derived from clay.

We find that a matte texture can not be produced in this type of a glaze with less than 0.15 equivalent of CaO. No other oxide can take the place of CaO in this, not even MgO.

(*b*) To be reliable under ordinary variable firing conditions, the glaze must contain the constituents necessary to produce a clear glossy glaze at two or more cones below the maturing point of the matte glaze when the Al_2O_3 has been decreased to an equivalent compatible with the heat treatment given.[3]

The equivalent of PbO in the medium and low fire matte glazes should not be less than 0.5, the zinc oxide should not exceed 0.1, and the equivalent of SiO_2 should be such that, with the reduced Al_2O_3, the oxygen ratio would be 2.0.

TYPE II. RAW GLAZES WITH LOW LEAD AND CONTAINING BARIUM.

(*a*) In these glazes there can be less Al_2O_3 and CaO.

(*b*) The SiO_2 content is more a function of glost heat treatment than of molecular proportions of the other oxides.

THEORIES AS TO CAUSE OF MATTENESS.

After studying many series of glazes which were made to determine the limiting proportions and conditions in the development of matte glazes, we concluded that matteness was *not*

[3] Illustration of this may be found in the case of Professor Orton's glaze No. 58, Trans. A. C. S., Vol. X, p. 557. He started with the following cone 4 glossy glaze:

$$\left.\begin{matrix}0.4\ PbO\\0.2\ K_2O\\0.2\ CaO\\0.2\ ZnO\end{matrix}\right\}\ 0.35\ Al_2O_3,\ 2.56\ SiO_2$$

and finally arrived at the formula

$$\left.\begin{matrix}0.4\ PbO\\0.15\ K_2O\\0.45\ CaO\end{matrix}\right\}\ 0.4\ Al_2O_3,\ 1.6\ SiO_2$$

which he said was a very pretty matte in patches and flowed fairly well. Had he proceeded contrary to some of his earlier conclusions and increased the PbO at the expense of ZnO and then reduced the silica, he would have obtained a far better matte, one that would have had a longer heat range. Or had he started with the following more fusible glaze as a base he would have obtained a cone 4 matte by merely increasing the Al_2O_3:

$$\left.\begin{matrix}0.5\ PbO\\0.20\ CaO\\0.20\ K_2O\\0.10\ ZnO\end{matrix}\right\}\ 0.2\ Al_2O_3,\ 1.6\ SiO_2$$

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due *per se* to (1) low oxygen ratio, (2) high aluminium content, (3) immaturity, (4) crystallization, or to (5) "overloading."

That these conclusions are true can be easily shown:

(*a*) That a matte texture can not be produced by merely decreasing the oxygen ratio has been shown in every fully reported study on matte glazes.[4]

(*b*) No matter what oxygen ratio a glaze may have, a mere increase in Al_2O_3 will not always result in a matte texture or even in matteness.[5] With many RO combinations, an increase in Al_2O_3 would result either in blistered glossy glazes or in dry surface effects.

(*c*) Immaturity will not produce a matte texture in every glass, for if it would, we would have a matte texture at some stage of the development of every glaze.[6]

(*d*) Matteness in this type of a glaze cannot be due wholly, if at all, to crystallization.[7] Unsuccessful attempts have been made to produce mattes by crystallization in these glazes through additions of ZnO. In no matte glazes made upon the usual formula proportions of raw lead glazes, *i. e.*, with 0.2 or more Al_2O_3, has there been found sufficient crystallization to produce the "all over matte texture" sought for in matte glazes.[8] The maximum crystallization found in several matte glazes did not exceed 2 per cent. by volume of the entire mass. That matte effects may be produced by crystallization was shown by Purdy and Krehbiel,[9] but the surfaces of these glazes were rough, quite unlike the usual matte surface.

(*e*) If matteness is due to "overloading" *per se*, we should be able to cause matteness by overloading with SiO_2, clay, or calcium. Overloading with SnO_2 will increase the tendency towards matteness, but a matte effect can not be produced in every mixture by this means.

[4] Compare this statement with that made by Binns, Trans. A. C. S., Vol. XII, p. 541, 542.

[5] Compare this statement with those by Mayer and Hattinger, Trans. A. C. S., Vol. X, p. 579. They differ with Orton, p. 574 and with the present statement.

[6] Compare with Orton, Trans. A. C. S., Vol. X, p. 574.

[7] This is in agreement with Professor Orton, Trans. A. C. S., Vol. X, p. 574.

[8] Compare this with Claflin, Trans. A. C. S., Vol. XII, p. 539, and with Stull, Trans. A. C. S., Vol. X, p. 581.

[9] Trans. A. C. S., Vol. IX, p. 319.

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Our Working Theory.—Our working theory as to the cause of matte texture in such glazes as are described as Type I is that normatively there must be a glassy matrix in which a substance, or substances, is slowly forming and dissolving.

We theorize on the normative basis that anorthite feldspar ($CaO\ Al_2O_3\ 2SiO_2$) and leucite ($K_2O\ Al_2O_3\ 4SiO_2$) are the mineral materials which, by their *gradual formation* and *solution*, produce this matte texture in most cases. The presence of orthoclase aids in the retarded formation and solution of anorthite and leucite, and perhaps behaves to some extent in somewhat the same manner and with the same result.

We know that if sufficient orthoclase is added to cause a portion of the calcium to react with it rather than with clay, thus tending to form leucite ($K_2O\ Al_2O_3\ 4SiO_2$) rather than anorthite, we will have the same general effect and one that is less apt to appear scummy.

Our data show further that according to our working theory an increase in wollastonite ($CaO\ SiO_2$) content will shorten the heat range in which a glaze will remain as a matte but will lengthen the heat range in which it will remain as a good glossy glaze. It seems necessary, however, to have some wollastonite present in matte glazes (especially if the PbO is as low as 0.5 equivalent) or the glaze will be dry.

Illustration of Glazes of Type I.—(A) The following is a glossy glaze at cones 03 to 1. Neither whiting nor clay is used in making this glaze.

$$\left.\begin{matrix} 0.75\ PbO \\ 0.15\ K_2O \\ 0.10\ ZnO \end{matrix}\right\} 0.15\ Al_2O_3,\ 1.7\ SiO_2$$

The normative constitution of this glaze is calculated to be:

0.375 equivalent $2PbO, SiO_2$
0.05 equivalent $2ZnO, SiO_2$
0.15 equivalent $K_2O, Al_2O_3, 6SiO_2$
0.125 equivalent SiO_2

By adding 0.2 equivalent of anorthite to this mixture we obtain a glaze having the following empirical formula:

$$\left.\begin{matrix} 0.60\ PbO \\ 0.12\ K_2O \\ 0.08\ ZnO \\ 0.20\ CaO \end{matrix}\right\} 0.32\ Al_2O_3,\ 1.58\ SiO_2$$

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Experience has shown that this will be a good matte glaze.

(B) A glossy glaze of the following formula, 0.55 PbO, 0.15 K_2O, 0.30 CaO, 0.2 Al_2O_3, 1.675 SiO_2, will have a normative constitution as follows:

0.275 equivalent $2PbO, SiO_2$
0.15 equivalent $K_2O, Al_2O_3, 6SiO_2$
0.05 equivalent $CaO, Al_2O_3, 2SiO_2$
0.25 equivalent CaO, SiO_2
0.075 equivalent SiO_2

We found that this glaze had a heat range as a glossy glaze from cone 03 to 6.

By increasing the Al_2O_3 of this glaze to 0.35 equivalent through additions of clay, we would obtain a glaze having the following normative constitution:

0.275 equivalent $2PbO, SiO_2$
0.15 equivalent $K_2O, Al_2O_3, 6SiO_2$
0.20 equivalent $CaO, Al_2O_3, 2SiO_2$
0.10 equivalent CaO, SiO_2

This glaze has a heat range as a matte from cones 03 to 6, the same as the glossy base glaze. It has a tendency to scum.[10]

(C) A good matte glaze that will not scum and has a heat range from cones 05 to 4 may be made as follows:

0.575 PbO
0.200 CaO } 0.35 Al_2O_3, 1.6 SiO_2[11]
0.225 K_2O

The normative constitution of this glaze is

0.2875 $2PbO, SiO_2$
0.125 $CaO, Al_2O_3, 2SiO_2$ (anorthite)
0.04375 $K_2O, Al_2O_3, 6SiO_2$ (orthoclase)
0.18125 $K_2O, Al_2O_3, 4SiO_2$ (leucite)
0.075 CaO, SiO_2 (wollastonite)

It should be noted that while this glaze has, according to norm calculations, less anorthite than the preceding ones, it contains considerable leucite resulting from the reaction of calcium and feldspar. Glazes in which this reaction is prominent, as in this case, are whiter, clearer glazes, freer from that scummy or soapy appearance, and are much less soluble.[12]

[10] See also Binns' Glaze 4, Trans. A. C. S., Vol. V, p. 52.

[11] See Binns' Glaze 11–4, loc. cit.

[12] It should be noted also that in no matte glaze was any free SiO_2 found by this method of calculation.

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Examples could be multiplied in illustration of the sort of mixture in which we have this retarded formation and solution phenomenon, but enough has been given to illustrate the case. Every matte glaze we have obtained exhibits these same normative phenomena and relations.

This retarded formation and solution results in or is conditioned by (1) low oxygen ratio, (2) high Al_2O_3 content, (3) immaturity, (4) crystallization, and (5) overloading; but all of these are either the effect or the result from a common cause. The condition, according to this theory, that causes a matte texture in these glazes is a glassy matrix so constituted as to permit of slow formation and solution of some one or more of the feldspars.

We are convinced of the soundness of this theory by the fact that whenever we have *rapid solution* we have evidence of boiling and blistering at one and the same time with fair gloss. In cases of *delayed solution*, as in case of glazes rendered dry through addition of clay, the glaze passes directly from the dry to the glossy conditions without showing matteness as an intermediate effect. It is only with *retarded* formation and solution of these feldspars that we have matteness through a reasonable heat range.

All matte glazes of this type (raw lead, no barium) show a matte fracture throughout their mass. They appear to be full of bubbles that do not come to the surface. In some cases a fracture actually shows a honey-combed structure, hence it may be that, owing to slowness of the solution, the gases which cause these bubbles are not formed so rapidly, *i. e.*, the boiling is less violent, hence they do not show on the surface. Aside from the bubbles, however, we have globular like material. One naturally would hesitate to argue from the presence of these globules and from the retarded solution of these feldspars, that matte glazes are examples of what Staley[13] calls mineral emulsions yet, in effect, this emulsion idea seems to fit the case.

Conclusion as to Cause of Matteness in Glazes of Type I.—(1) To produce a matte glaze of this type this theory states that it is necessary to have about

[13] Trans. A. C. S., Vol. XIII, p. 679.

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0.25–0.30 equivalent $2PbO, SiO_2$
0.10 equivalent CaO, SiO_2

to which shall be added about 0.35 equivalent of the feldspars.

(2) It is necessary that a large portion of these feldspars shall have a tendency to be formed during the fusion.

(3) The proportion of the feldspar that must necessarily be thus slowly formed during the fusion is dependent upon the kind. If anorthite is to be the only feldspar that would be formed if the fusion is carried to completion, it should constitute about 0.2 out of the total of 0.35 equivalent of the feldspars. If we take it that leucite is to be thus slowly formed with anorthite, the total number of equivalents of slowly forming feldspars must be increased to 0.30 equivalent.

(4) Example:

0.28 equivalent $2PbO, SiO_2$	The lead glass
0.10 equivalent CaO, SiO_2	
0.10 equivalent leucite	The feldspars
0.20 equivalent anorthite	
0.10 equivalent orthoclase	

The empirical formula of this mixture would be

0.528 PbO
0.189 K_2O } 0.377 Al_2O_3, 1.67 SiO_2
0.283 CaO

TYPE II. LEAD-BARIUM MATTES.

It is well known that barium forms silicates very slowly but that when barium is thus combined it becomes almost as good a fluxing agent as lead oxide. When barium is used with low lead we know that the glaze fuses very slowly, hence, instead of a slowly forming and slowly dissolving solute, we assume in this theory that we have, in this case, a slowly forming solvent, the net result of which is the same sort of a retarded formation and solution as in case of the glazes of the first type.

A matte texture, other than those formed by crystallization or by artificial roughening of the surface, can be produced only on the basis of this theory of retarded formation and solution. We use this expression "retarded solution" to contrast this phenomena with such "arrested or delayed reactions" as we have

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in the case of a sillimanite solute which would produce dry surfaces rather than mattes.

Our theory does not say that these feldspars are being formed, although we believe this to be the case. Our theory is offered as a very practical working basis.

SUPPLEMENTARY NOTES.

(1) To produce either of these types of matte glazes it is not necessary to dip especially thick[14] or to cool slowly,[15] nor do they require the use of gum of tragacanth or other glues to make them adhere properly to the tile and to burn without parting. In fact a properly constituted matte glaze need not be applied in any way different from the glossy glazes.

(2) To produce water marking or partings, it is necessary to use a constituent that will raise the surface tension of the glaze. Drying cracks, due to thick dipping, may control the character and extent of these partings, but it is the composition of the glaze that causes it to crawl and then to partially fuse and flow back into the place where these drying cracks appear.[16] Zinc oxide and CaO are very serviceable in this connection.

DISCUSSION WRITTEN AFTER READING THE PAPER.

Mr. Pence: I am pleased to note that Prof. Purdy, in developing a theory for cause of matteness in the two matte types recognized by him, has arrived at conclusions that agree fundamentally with my own as set forth elsewhere in this volume. We seem to have viewed the same phenomena from somewhat different angles, but the testimony in the two cases should be considered confirmatory rather than contradictory.

In the case of Prof. Purdy's Type I, or high PbO matte, the cause of matteness is assigned to the slow formation and solution of one or more of the feldspars, the action taking place within a glassy matrix. This idea of formation I consider to be analogous to my own idea of segregation since Prof. Purdy's

[14] Compare this with statement by Binns, Trans. A. C. S., Vol. X, p. 580.

[15] See Trans. A. C. S., Vol. X, p. 582.

[16] See discussion on this point in Trans. A. C. S., Vol. XI, p. 170. Scaling of the glaze off of the ware was there confused by some with the water marking and parting shown in many matte glazes.

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assumption that the compounds formed are slowly dissolving includes the requirement that they be present in some undissolved or segregated form following the act of their formation.

Prof. Purdy lays no emphasis upon the idea of segregation or precipitation in the glaze. In fact he speaks disparagingly of the theory of crystallization. It is seen, however, that the fundamental idea of segregation necessarily underlies his theory for mattes of Type I.

In my conclusions on a theory for cause of matteness, I have not presumed to say what compounds were formed or segregated.

I have not considered the point of slow solution to be of great importance, although, undoubtedly, such solution is taking place under the conditions that obtain in the maturing of the glaze.

In Type II, or lead barium mattes, the basis of explanation given is practically identical with my own, *viz.*, the retarded combining action of the barium.

Prof. Purdy has not given recognition to the zinc crystal type of matte at medium fire. This is not surprising for such mattes in all probability would rarely be produced successfully in the small experimental kiln.

Mr. Purdy: Having no knowledge of the possibility of precipitation of amorphous material from igneous solution, and having seen no case in which such a physical action was apparent, I cannot deny the possibility of such an occurrence. I must say, however, that such a reaction does not strike me as being possible. The only cases of "separating out" that I have recognized was that of crystalline material. I did not realize that I had spoken disparagingly of the theory of crystallization as cause of matteness, except in the cases discussed. The facts are that we have produced very pretty crystalline matte glazes, but most matte glazes produced commercially and most of those which have heretofore been described before this Society were neither crystalline nor had any possibility of being crystalline under any ceramic kiln condition.

I can not see that our theory of "slow formation and slow solution of the feldspar norms" is fundamentally in agreement

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with Mr. Pence's precipitation theory. He must assume complete formation, a saturated solution and a precipitate of a compound having definite physical properties. We hold, on the contrary, that in matte glazes (other than those which are crystalline) we have incomplete reactions both chemical and physical, that the question of saturation of igneous fusions is one of attending physical conditions on which the production of matte texture is not necessarily conditioned, and that when the precipitate has definite physical properties the "mother glass" is more likely to be glossy than matte unless nearly the entire glaze has crystallized.

Mr. Pence considers that the reactions are completed and the undissolved substance has been precipitated from solution. We consider that the reactions have not been completed and the undissolved material had never been in solution.

The only case which he cites which seems to give more credence to his views than to ours is that of a glaze which had previously been melted as frit and dropped into water, and which, when applied and re-fused as a glaze had a matte texture, notwithstanding the fact that as a frit it was a clear glass. I have never personally seen such a case but do not in the least doubt that his observations are true. We have fritted a large portion of matte glaze batches to clear glassy fritts and then, after mixing with the unfritted portions into glazes, have found that we had a better matte both as to texture and heat range. This experience, in substance, is of the same sort as that recited by Mr. Pence.

In such cases as these, it seems more plausible and more in keeping with known laws of fusion to believe that in these clear frits which have been suddenly cooled there is complete solution without complete reaction and that when re-fused as a glaze opportunity is given for these reactions to take place. I say that this conception is more plausible than that in these frits the chemical reactions had been completed and, when refused as a glaze, amorphous compounds precipitated out from solution.

If the procedure which Mr. Pence's theory described is true, all mattes should be crystalline. The procedure which my theory described involves a conception of a solution like unto an emul-

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sion. As I said, I hesitate to say that matte glazes are examples of rigid emulsion although they have every appearance of being such. Since most matte glazes are not due to crystallization, I can not see how Mr. Pence's conceptions can be considered plausible. His theory applies only to the crystalline mattes, while the theory I present is, as I stated, applicable only to the non-crystalline matte glazes.

A typical crystalline matte glaze is of the kind Mr. Pence calls zinc mattes. Of these we have made many in our laboratory but classified them as crystalline glazes in which conditions had not been correct to permit of the growing of large crystals. Such glazes were described by Worcester in Vol. X, p. 450, of our Transactions, and a very pretty discussion of these by Prof. Stull may be found in Vol. VI, p. 186.

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A THEORY FOR THE CAUSE OF MATTENESS IN GLAZES.

By FORREST K. PENCE, Zanesville, Ohio.

CLASSIFICATION OF MATTES.

Experience with a great variety and widely varying types of matte glazes, both in experimental research and in commercial control, has impressed me more and more with an idea regarding the cause of matteness in glazes. This idea has gradually developed into a conviction which I choose to call a theory, as set forth in the following.

It is necessary to state at this point that glazes whose matteness depends upon their content of barium form an exception in their action to the general class of matte glazes. The barium glazes will therefore be discussed under a separate classification.

We may therefore divide matte glazes into two classes.

In the first and more general class (which in this paper we shall call "Class A"), the formation of the matte texture is due to a phenomenon which is analogous to the chemical precipitation which occurs when certain salts are brought together in aqueous solution.

To illustrate: When sodium sulphate and barium chloride are brought together in water the formation of an insoluble salt, barium sulphate, is made possible by the liquid medium. Therefore, according to the law that when an insoluble compound can be formed it will be formed and precipitated, the solid, barium sulphate, is formed throughout the solution.

Now in a matte glaze the fluid matrix, of which Purdy speaks, plays practically the same rôle as does the water in the above illustration in facilitating precipitation; and when, in excess of this fluid matrix, the elements are present in proper proportion to form an insoluble compound, such a compound will be formed and its precipitation facilitated throughout the mass.

We shall divide Class A matte glazes into two sub-divisions.

First. Those whose matte texture is evidently due to the formation of a calcium alumina compound. In these glazes the CaO is 0.2 to 0.35, Al_2O_3 is 0.30 to 0.35, O. R. is $1 : 1^1_{,2}$.

Second. Those in which the texture is determined by the for-

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mation of a zinc compound. In these glazes ZnO is 0.30 to 0.50, Al_2O_3 is 0.1 to 0.2, O. R. may be as high as 1 : 2.

The second class of matte glazes (which we shall call "Class B") owe their matte texture to the presence of materials that enter into combination or solution slowly and with difficulty. Most prominently under this heading would be placed the barium mattes. The use of tin oxide as an aid to matteness would probably conform to this class. This class includes the glazes that have been commonly called "mattes of immaturity."

CLASS A MATTES.

First Type.—In considering the glazes of the first division of Class A, the following experiments will be of interest:

Of the type glaze X

$$\left.\begin{matrix} 0.55\ PbO \\ 0.15\ K_2O \\ 0.30\ CaO \end{matrix}\right\} 0.35\ Al_2O_3,\ 1.6\ SiO_2$$

the following portion was fritted.

$$\left.\begin{matrix} 0.15\ PbO \\ 0.15\ K_2O \\ 0.30\ CaO \end{matrix}\right\} 0.35\ Al_2O_3,\ 1.3\ SiO_2$$

The raw addition was 0.4 PbO, 0.0 Al_2O_3, 0.30 SiO_2.

All frits were prepared by the crucible method in a small gas and air blast furnace. The frits were all clear, transparent glasses, care being taken to make the fritting process thorough. The frit and raw addition were then ground together in a ball mill and dipped on white wall tile bisque. The tiles were then fired to cone 02. The resulting glaze was a matte of texture practically identical with that produced by the same glaze compounded from the raw materials.

Two frits were then prepared which included the entire glaze batch.

Frit Y		Frit Z	
0.55 PbO 0.15 K_2O 0.30 CaO	0.35 Al_2O_3, 1.6 SiO_2	0.50 PbO 0.15 K_2O 0.35 CaO	0.35 Al_2O_3, 1.6 SiO_2

The frits were clear, transparent glasses.

These ground frits, applied to wall tile bisque and fired at

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cone 02, gave mattes that were practically identical respectively with the raw matte glazes of the same formulae.

This would seem to be very good evidence that some materials which had been taken into solution in the clear, transparent, glassy frits were precipitated, *i. e.*, separated out, probably as some definite compound, at the temperature suitable for the precipitating or crystallizing action to occur. What the compound or compounds may be has not as yet been determined.

In Sprechsaal for 1911, No. 50, p. 730, is given a list of calcium aluminates and calcium alumina silicates with their respective melting points. We may choose possible compounds from this list in explaining the matte texture development, but positive identification is a task for the expert petrographer.

It should be pointed out that the precipitating action may be, in general, a gradual and continuous process, so that in no period of the matte development of the glaze in the kiln does the glaze necessarily pass through a stage of brightness.

Second Type.—In considering the glazes of the second division of Class A, we shall only call attention to a phenomenon which doubtless others have observed. A zinc matte glaze when fired in one portion of the kiln showed a bright field with irregular clusters and masses of crystals distributed over it; but the same glaze was a uniform, silky, matte when it came from that portion of the same kiln which received a slightly higher heat treatment. However, no individual crystals could be distinguished by the naked eye. It is very probable that the crystallizing agent here is a zinc silicate compound. The identification of this compound is a subject for future study. The presence of small amounts of zinc, as 0.10 ZnO, in glazes of the calcium alumina type very probably functions simply as a flux and has no crystallizing action.

CLASS B MATTES.

To illustrate the glazes of Class B, or barium mattes, three glazes were prepared, each having the formula:

$$\left.\begin{matrix} 0.250\ BaO \\ 0.500\ PbO \\ 0.075\ CaO \\ 0.175\ KNaO \end{matrix}\right\} 0.33\ Al_2O_3,\ 2.0\ SiO_2$$

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The method of introducing the BaO differed in the three glazes as follows:

G_1. BaO introduced as barium carbonate.

G_2. BaO introduced as barium oxide, which was prepared by igniting barium nitrate.

G_3. BaO introduced was incorporated in a frit of formula:

$$\left.\begin{matrix} 0.175\ Na_2O \\ 0.175\ K_2O \\ 0.150\ CaO \\ 0.500\ BaO \end{matrix}\right\} 0.15\ Al_2O_3,\ 1.45\ SiO_2$$

Results at cone 02:

G_1. Shows a dead matte texture.

G_2. Is an immature bright glaze.

G_3. Is similar to G_2.

This result is in accordance with common experience in replacing $BaCO_3$ in a glaze similar to G_1 with barium introduced in fritted form. The results indicate that the matteness in glazes similar to G_1 is due to the delayed fluxing action of $BaCO_3$, which in turn is probably due to the delayed and slow decomposition of the same.

$BaCO_3$ may also be introduced in small amounts as an aid to matteness in glazes of the other types. A small amount, as 0.04 BaO, introduced as $BaCO_3$ in glazes of Class A, will often prevent bright edges where the glaze is thin and its texture changed through attack of the body. This is further evidence that $BaCO_3$ in such cases promotes matteness in much the same way as tin oxide develops opacity in bright glazes.

On the other hand a glaze high in zinc (0.40 ZnO) with barium (0.25 BaO) substituted for lead, with low alumina (0.20 Al_2O_3), and O. R. 1 : 2, with rather prolonged firing treatment at cone 7, may give a matte of the zinc crystal type, showing that in a glaze of this type and treatment the barium has entered into combination and served as a flux.

We thus see that the use of certain materials is not restricted to glazes of any single type. However, the characteristics of the different types are distinct.

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SUMMARY AND CONCLUSION.

In explaining the development of matte texture in glazes we recognize two distinct classes.

In the first and more general class, the matteness is produced by the development of a fluid medium in which is facilitated the formation and precipitation or segregation of certain compounds difficultly soluble in this medium.

We have divided this class into two types.

In the first type the compound or compounds thus segregated are apparently calcium aluminates or calcium-alumina silicates.

In the second, the compound is apparently a zinc silicate.

This view explains why glazes of the first type should contain high Al_2O_3 and those of the second, low Al_2O_3. It also explains why there should be at least 0.50 PbO in raw glazes of this class, for why should PbO be so high if matteness depended simply upon the resistance of some compound to solution.

In the second or somewhat special class, the matteness is due to the retarded combining action and solution of an essential portion of the glaze. This class includes particularly those glazes whose matteness is due to the presence of $BaCO_3$ in the batch. These glazes may be termed "mattes of immaturity." This explains why in them the content of PbO required is, in general, not so high as in other mattes.

As previously stated, my regard for the theory set forth in this paper has developed with my experience in the commercial control of matte glazes and various simple glaze experiments. Proof can be established and compounds identified only by extensive study along chemical and petrographical lines.

The terms "Mattes of Crystallization" and "Mattes of Immaturity" are familiar to us from the experience of others. It has been my purpose to formulate the evidence at hand into a theory of general explanation which should be in harmony with commercial experience and with chemical law.

DISCUSSION.

Professor Staley: I believe it is true that matteness can be produced by crystallization; but I also believe that the number of mattes due to this phenomenon is very limited. I am con-

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vinced that a large number of mattes are classed as crystalline in which there are but few crystals and in which the matteness can be shown to be due to causes other than crystallization. I base my belief on the microscopic examination of a number of matte glazes, as will be reported in another paper at this meeting.

Mr. Purdy: I would like to ask if he believes in the formation of some compound within the glaze.

Professor Staley: I believe that in the true crystalline matte there is some compound formed; I think it separates as crystals.

Mr. Hottinger: I would like to ask Professor Staley if he ever made frits of the matte glazes. I ask this because my experience with matte glazes show that most of them when fritted in saggers and allowed to cool in the kiln show a crystalline separation. The crystals vary in shape depending on the bases used. The foregoing statements apply to glazes rather high in lead, from four-tenths equivalent up. With other matte glazes, such as barium, I have not been able to detect any crystals.

Professor Staley: I am not saying that matteness cannot be produced by crystallization, but what I am saying is that in the type of matte of which Professor Purdy was speaking this morning, the type generally known as immature, there has not been developed any appreciable amount of crystals. If you take that same composition and frit it, you may get matteness due to crystallization.

Mr. Hottinger: This would seem to indicate that the mattes are due to crystal formation, something separating from the glaze.

Professor Staley: As I say, it is possible to produce mattes by crystallization, but I have examined twelve different commercial mattes of many types and found very little separation of crystals in most of them.

Professor Binns: I want to ask Mr. Pence whether those frits that he made were poured into water to cool.

Mr. Pence: They were.

Professor Binns: They were thus cooled suddenly, of course, and present the appearance of glass. Then the same frits put upon tile and burnt exhibit a matte texture. How do you account for this change? Why is the frit transparent, when cooled quickly, and opaque when relatively slow-cooled?

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Mr. Pence: I think that is a point which substantiates my contention, that the material may be first taken into solution as in the frit, and in rapidly cooling the frit we retain it in the solution. But when the frit, ground and applied as a glaze coating, is put into the kiln, and subjected to continued heat treatment, we give the materials an opportunity to segregate, and thereby materials formerly in solution separate from the solution to form the matte texture.

Professor Staley: I would like to ask Mr. Pence if he thinks that the material has separated in the crystalline or amorphous state.

Mr. Pence: That is a point that remains undetermined. I contended myself with stating that it was segregation, because I had no way of knowing whether it was amorphous or crystalline, but I am inclined to think that it may be amorphous in some cases.

Professor Staley: I doubt very much whether amorphous material would separate from the glaze. I have worked with glass in rather a large number of cases, and I have never seen amorphous material separate from a glass.

Mr. Pence: I want to ask Mr. Staley if he had in mind the calcium alumina type of glaze when speaking of mattes due to immaturity.

Professor Staley: Yes.

I think if you take that same matte and frit it, you might get matteness, but the matteness would be due to altogether a different cause. I would like to examine, under the microscope, one of your raw mattes and one of your fritted mattes to see if the cause of the matteness in the two cases is different or not. There is no use in guessing when we can determine the facts with absolute accuracy.

DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Mr. Pence: The result in the case of the fritted matte shows that segregation in such a glaze is possible. The action of the glaze in the large commercial kiln as compared with its action in the small test kiln, the apparent evidences of segregation when the glaze is applied as a heavy coating and fired in the large kiln.

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and other experiences in the handling of these glazes, as suggested in Mr. Hottinger's remarks, point to segregation as an explanation of the matteness obtained.

Of course, there may be glazes abnormally high in Al_2O_3 or CaO, or abnormally low in PbO, the same being called mattes, whose texture would be due to immaturity.

The next addition to the evidence already at hand should be that provided by microscopic study. This will be presented at another time.[1]

Mr. Hottinger: As I have said before in the discussion of other papers bearing on this subject, I believe that matte glazes are due to crystallization. I refer more particularly to the high lead fritted glazes with which I have done considerable work.

To make a fritted lead matte glaze it does not seem necessary to have any fixed amount of lime or zinc as sometimes stated, for instance, a glaze of the following formula:

$$\left.\begin{array}{l} 0.67\ PbO \\ 0.03\ ZnO \\ 0.075\ CaO \\ 0.175\ Na_2O \\ 0.050\ K_2O \end{array}\right\} Al_2O_3,\ 0.28,\ 0.36,\quad SiO_2,\ 1.85$$

will produce matte glazes of various textures depending on Al_2O_3 content. With the higher content of Al_2O_3 a rough crystalline texture is produced, while with the lower content a rather smooth good glaze will be obtained. As will be noticed, the glaze has very little lime and zinc.

A frit made of this formula, when allowed to cool in the crucible, will show clear glass with small white spots; these spots, when examined with a glass, are seen to be needle-like crystals radiating in all directions from a common center.

By changing the formula and substituting lime for lead, the shape of the crystal changes; instead of being long needle-like they now are shorter and spread in fan shape.

It will be observed that the above facts confirm Mr. Pence's theory, as applied to fritted glazes, except that he calls it a pre-

[1] In this connection, see "The Microscopic Examination of Twelve Matte Glazes," this volume.—EDITOR.

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cipitation or segregation, and if only finished glazes on tile are taken for consideration, this would be the natural conclusion.

I have seen but few glazes on tile which by direct examination could be called crystalline, but when making them up as a frit and allowing them to cool slowly can, as a rule, find crystal segregations. My experience with high zinc glazes is limited and the few that I have observed I would class as crystalline, as surface indications of crystals, or, as it might be termed, incipient crystallization. With the barium matte glazes, I can only say that in practice my results agree very closely with the facts as observed by Mr. Pence, namely, that they are mattes of immaturity.

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THE MICROSCOPIC EXAMINATION OF TWELVE MATTE GLAZES.[1]

By HOMER F. STALEY.

INTRODUCTION.

This investigation consists of a study of the surface and internal structure of various types of matte glazes by means of the microscope. It was undertaken with the expectation that such a study would throw light on the cause of matteness in the various types and, therefore, enable us to set about producing a given kind of matte in a systematic manner.

In making the microscopic examination, the writer was very fortunate in securing the aid of Professor W. J. McCaughey, of the Department of Mineralogy, Ohio State University. Professor McCaughey has but recently come to the university from the government service at Washington. In that service, he was widely known as one of the most expert men in the country in the use of the microscope, especially in connection with microscopic examination of soils. I take this occasion to publicly thank Professor McCaughey for his part in the preparation of this paper.

DESCRIPTION OF SPECIMENS.

The following is a detailed description of the various samples examined:

I. TECO WARE.

The specimen of glaze examined came from a small green vase, bearing the Teco mark. As it appeared on the ware, it was a green matte of very pleasing shade and texture. The composition is unknown.

Under even a low-power glass, this glaze is seen to consist of two layers, an upper layer of crystals and a lower glossy layer. The surface of the matte is composed entirely of large (microscopically speaking), elongated crystals. These crystals interlace, forming a texture not unlike that recognized by petrographers as ophitic. An example of this texture is frequently found in diabase. These crystals very frequently form penetration twins with an angle of about 60°. The intersal space of the

[1] Contribution from the Ceramic Engineering Laboratory of the Ohio State University.

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crystal layer is free from glass, which seems to exist only below the surface.

These large crystals are about 0.07 by 0.5 mm. in dimensions. They are green in color and are weakly birefringent. Occluded in the crystals is a considerable proportion of extraneous matter. This occluded matter is a confused aggregate that does not render itself to the ordinary methods of microscopic crystal determination, even with a glass that gives 600 to 700 magnifications. It is, however, probably amorphous. It may possibly but not probably be a conglomerate mass of infinitely small crystals. The surface of these crystals presents the characteristic surface of impure crystals, that is, they have a rough appearance.

Beneath the layer of crystals and surrounding the lower projections of the crystal layer is a layer of glass. This glass is perfectly clear and is of the same shade of green as the large crystals.

As a matter of interest, although it has no connection with the matte texture, we may state that in the glass itself there has been developed a second generation of microscopic crystals. These are seen under a high-power objective to show fairly high birefringence and positive optical elongation. They were very small and roughly oblong in shape.

The matte texture in this sample is due to two factors. First, the presence of the crystal layer on the surface. Second, the rough surface, due to the occluded matter, of the crystals composing this layer.

II. ROOKWOOD VELLUM GLAZE.

The specimens were taken from some sherds of glaze and engobe that had come from a small piece of ware. These showed the characteristic beautiful misty effects on the underglaze decoration that has been so much admired in this ware. Of course, the composition of the glaze is unknown.

Microscopic examination shows that the surface of the glaze is characterized by a crinkled appearance not unlike that of a withered apple. The crinkles are not systematically arranged, but run in all directions in a very irregular manner. This appearance would be due, probably, to a contraction of the body of the glaze after the skin or surface had partly set. The more

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prominent of these crinkles are evidently what have been mistaken for crystals by some observers using hand glasses. Distributed throughout the glaze are a large number of large blowholes or bubbles, about 0.4 mm. in diameter. These are easily seen by the unaided eye and are what give the glaze the finely mottled appearance. Many of these bubbles are entirely submerged in the glass. Others were in the process of bursting when the glaze became rigid. Still others have unquestionably broken and disappeared. While it is not at all the function of this paper to account for the production of the various types of matte textures described, we suggest that the loss of gas bubbles would be one circumstance that would make the body of a glaze contract in an irregular manner more than a partially rigid skin.

There has been a slight development of extremely small crystals in this glaze. They are diamond shaped and only about 0.005 mm. in diameter. The total amount formed is less than 1 per cent. of the volume of the glaze. There is also found in the glaze approximately 10 per cent. of a confused mass of material showing aggregate polarization. This leads us to state that it is undissolved material. This material and also the crystals are embedded in the glass. This indicates that they have no effect on the production of the matte surface. The matte surface is not at all confined to the areas showing undissolved matter or crystals. The matte effect is due to the finely crinkled surface of the glaze.

III. PROFESSOR ORTON'S MATTE.

This specimen was taken from trial piece 178 in Professor Orton's article on matte glazes in Vol. X, Transactions of the American Ceramic Society. The formula of this glaze is:

$$\left.\begin{matrix} 0.15\ K_2O \\ 0.10\ PbO \\ 0.10\ ZnO \\ 0.35\ CaO \\ 0.30\ BaO \end{matrix}\right\} 0.233\ Al_2O_3,\ 1.90\ SiO_2$$

The sample was fired to cone 2. Professor Orton used this glaze raw. This particular sample was chosen from those available because of the small but well developed "water markings."

Under the microscope, the characteristic feature of this

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glaze is a high percentage of a conglomerate mass of material that shows weak aggregate polarization. These features show that this material is undissolved matter. The interior of the matte shows a granular texture. This texture is seen under a high power to be due to a very even distribution of the undissolved matter.

The surface of the matte is inclined to be uneven, due to this undissolved matter. The amount of glass present is not great enough to conceal the unevenness of the surface that would be presented by the undissolved material alone. The higher parts of the surface are coated with a thin film of glass, while in the lower portions are little rivulets of smooth glass. These rivulets are what cause the "water marking." This type of matte is plainly due to immaturity.

IV. MINTON'S MATTE FOR TERRA COTTA.

The specimen was taken from a sample tile from the Perth Amboy Terra Cotta Co. This glaze was developed by Mr. Leroy H. Minton, while in the employ of the above firm. The particular tile chosen happened to be rose colored and was a good matte, smooth to the touch, and finely "water marked." The composition is unknown.

The microscope shows the surface of this matte to be roughly granular. This is easily seen by examination of a cross section of the glaze. The amount of glass in this matte is relatively small, 35 to 40 per cent. There does not seem to have been any development of crystals. The rest of the glaze, 60 to 65 per cent., is a heterogeneous mass showing aggregate polarization. These characteristics show it to be residual, undissolved matter. This undissolved matter is not evenly distributed as in Professor Orton's matte, but occurs in unevenly distributed masses. The result is that surface of the matte is more roughly granular than in Professor Orton's sample. The other features of the surface are the same as the sample from Professor Orton's series, and this matte is also due to immaturity.

V. VAN BRIGGLE MATTE.

The specimen was taken from a small blue vase bearing the imprint of the Van Briggle Art Pottery of Colorado Springs,

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Colorado. On the piece, the matte presents a very pleasing appearance, shows fine water markings, such as described as occurring on Professor Orton's sample, and feels smooth to the touch. The composition is unknown.

Microscopic examination shows this glaze to be of the immature type and very similar to the sample of Professor Orton. The proportion of undissolved material is about 60 per cent., and it is evenly distributed. Both the undissolved material and the rivulets of glass are blue.

VI. BROWER'S MATTE.

This sample was taken from a trial piece produced at the Ohio State University, Ceramic Engineering Department, by Mr. Fred W. Brower, under the direction of Professor R. C. Purdy. The formula of the glaze was:

$$\left.\begin{matrix} 0.55\ PbO \\ 0.15\ KNaO \\ 0.30\ CaO \end{matrix}\right\} 0.4\ Al_2O_3,\ 1.6\ SiO_2$$

The sample was fired at cone 1.

In appearance this glaze has the alligator hide effect. The surface is divided into slightly elevated areas about one-half inch square by rivulets of glass. From an artistic standpoint the effect is rather good.

This glaze is characterized by the very high percentage of undissolved material. This runs about 80 per cent. In addition to the usual nondescript undissolved matter found in the other mattes of this type, large particles of quartz are seen. These particles are fully 0.05 mm. in diameter and show angular edges, which indicates that they have not been acted upon to any large extent by the magma.

This sample falls very decidedly into the class of mattes due to immaturity.

VII. GRUBEY GREEN MATTE.

The specimen was secured from a large vase bearing the Grubey imprint. On the vase, the glaze had the green color and artistic rough matte appearance characteristic of this well-known ware. The composition of the glaze is not known.

The internal structure of this glaze is characterized by the

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presence of two glasses. One of these is very clear, clean-cut, glass, colored green. The other glass carries a very large percentage of undissolved material. This undissolved material consists of heterogeneous matter, such as found in the other mattes of the immature type, and also a considerable amount of what is apparently undissolved fine-grained quartz. Both glasses and the undissolved matter are colored green. No crystals have been developed.

The surface of this matte is not as uneven as that of some of the others examined and the percentage of glass present is higher. Therefore, the flow of the superficial glass film into the lower lying areas is not so much in evidence. The rough granularity of some of the immature mattes is replaced by innumerable little hillocks rising with gentle slope from the surface of the glass. This gives to the surface a rippling effect midway between the crinkled effect of the vellum glaze and the granular effect of the immature mattes carrying a high percentage of undissolved matter. Of course, in this discussion we are speaking about the minute texture of the surface. The rough irregularities of surface seen in a piece of Grubey ware are due to thickness of dip, running of glaze, etc. With these we have no concern.

We would, then, classify this matte as belonging to the immature class, but as having a rippled rather than a granular texture, due to the comparatively low percentage of undissolved material.

VIII. MISS COOKE'S COPPER MATTE.

This specimen was secured from one of a series of trial tiles produced by Miss M. E. Cooke in the Ceramic Engineering Laboratory of the Ohio State University. The trials were made under the direction of Professor Edward Orton, Jr. The particular sample used was chosen because of its beautiful green matte effect and, as it appeared to the unaided eye, its high state of crystallization. This was a raw glaze in which Cornwall stone was used in place of feldspar. The formula is as follows:

$$\left.\begin{matrix} 0.088\ KNaO \\ 0.344\ CaO \\ 0.475\ PbO \\ 0.093\ CuO \end{matrix}\right\} 0.50\ Al_2O_3,\ 1.466\ SiO_2$$

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To our surprise, we found that matteness in this sample is not due to crystallization but to the high percentage of undissolved material. The glaze consists of about 30 to 40 per cent. of green glass and about 60 to 70 per cent. of undissolved matter, also tinted green. The matteness and water markings are brought about in the same manner as in other mattes of the immature type.

The glass from the rivulets is perfectly clean and shows the development of a small amount of exceedingly small crystals. These crystals vary from hair-like to rod-like in shape. In size they are about 0.002 x 0.01 mm. They show negative optical elongation. From the fact that these few small crystals occur only in the clear glass and do not even roughen the surface of this, we know that they have no part in the production of the matte texture.

This matte also falls into the class of typical immature mattes.

IX. ROOKWOOD RED-BROWN MATTE.

The sample was secured from a small sherd of a vase of this ware. As it appeared on the piece, the glaze was a rather dull matte whose chief beauty is in the peculiarly attractive tint. The composition is unknown.

Examination of the interval structure of this glaze shows that it carries a very high percentage of undissolved matter, a large part of which is apparently iron oxide. In the glassy portion there has been developed a small growth of tiny needles about 0.002 x 0.01 mm. in size. From the study of the surface of the glaze, it is quite questionable whether these crystals have any part in producing matteness. The surface is coarsely uneven and irregular. Irregularity of surface which could be due to the development of these minute crystals would be a microscopic unevenness and would call for a much higher percentage of crystals than is actually found. The matteness is due to a coarse unevenness of the surface and is, in all probability, caused by the large quantity of undissolved material, as in the case of the other immature mattes.

We, then, catalog this matte as belonging to the class of immature mattes.

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X. KNOLLMAN'S MATTE.

This specimen was procured from a trial tile made by Mr. H. J. Knollman, in the Ceramic Engineering Laboratory, Ohio State University, under the direction of Professor R. C. Purdy. The appearance of the glaze on the ware is that of a smooth matte of dull luster and free from water markings. In cross section this glaze is, even to the unaided eye, plainly vesicular.

This is a fritted glaze carrying considerable barium, introduced as carbonate. The formula of the frit is:

$$\left.\begin{matrix} 0.140\ Na_2O \\ 0.138\ K_2O \\ 0.444\ CaO \\ 0.278\ BaO \end{matrix}\right\} 0.278\ Al_2O_3 \left\{\begin{matrix} 1.635\ SiO_2 \\ 0.438\ B_2O_3 \end{matrix}\right.$$

The formula of the glaze is:

$$\left.\begin{matrix} 0.126\ Na_2O \\ 0.124\ K_2O \\ 0.500\ CaO \\ 0.250\ BaO \end{matrix}\right\} 0.35\ Al_2O_3 \left\{\begin{matrix} 1.97\ SiO_2 \\ 0.394\ B_2O_3 \end{matrix}\right.$$

The sample was fired at cone 02.

Examination under the microscope with a high-power glass shows that this is a glassy glaze with little undissolved matter. The glass itself is characterized by the presence of innumerable small vesicles or bubbles. These are distributed throughout the glass. A large number have risen to the surface but have not penetrated the skin. By elevating the skin at a multitude of points, they have rendered the surface uniformly uneven.

The presence of a considerable quantity of barium carbonate in the batch of this glaze is in all probability an important factor in producing the matte. This chemical gives off a gas, CO_2, at high temperatures and also furnishes to the glaze a base, BaO, which is especially liable to attract sulphur. The effect of sulphur in causing a toughening of the skin of a glaze or enamel has been noticed by the writer and others.

We would classify this glaze as belonging to a class whose matteness is due to an irregular surface produced by numberless small vesicles elevating the skin of the glaze.

XI. HAMILTON MATTE GLAZE.

This specimen was secured from a large green jardiniere

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made in a small art pottery at Hamilton, Ohio. On the ware the glaze is a smooth matte, with rather more luster than the usual green matte. When the light is allowed to play on the surface, glistening particles are seen here and there. Under a good hand glass small, rod-like crystals are seen on the surface. The glaze has obviously been applied quite thin. Where the glaze has become thick by running into cavities or collecting in drops on the bottom of the piece, it is not matte but clear, dark green, glass.

On examination, we found that this glaze is a pure green glass containing no undissolved matter. There has been a large development of thin, rod-like, green crystals 0.02 x 0.10 mm. in size. For purpose of comparison, we may recall that the crystals in the "Rookwood Red Brown Matte" were 0.002 x 0.01 mm. and the large crystals in the "Teco Matte" were 0.07 x 0.5 mm. The crystals differ also from the occurrence in the "Rookwood Red Brown Matte" in that they are vastly more numerous and are not accompanied by any undissolved matter. They differ from the crystals in the "Teco Matte" not only in size but also in being free from occluded matter. The absence of this extraneous matter permits the crystals having the smooth surfaces characteristic of pure crystals. The small size of the crystals prevents the occurrence of large glistening patches, such as are found in a texture composed of large pure crystals.

The crystals occur not only embedded in the glass but projecting from it and lying on its surface, thus forming a structure similar to that of the "Teco Matte," but composed of much smaller units with brighter surfaces. The result is, as we would expect and have described, a smooth fine grained matte with rather high luster and an occasional bright glistening speck.

We unhesitatingly classify this matte as belonging to the class produced by a layer of small clean crystals.

XII. JACKSON'S BLACK MATTE.

This glaze is a clear green glass covered with a black skin with a metallic luster. It was made by Mr. E. C. Jackson.[2]

The formula of the glaze is:

[2] Trans. A. C. S., Vol. IX, page 408.

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$$\left.\begin{array}{l} 0.500\ PbO \\ 0.082\ K_2O \\ 0.100\ ZnO \\ 0.100\ CaO \\ 0.218\ CuO \end{array}\right\} 0.205\ Al_2O_3,\ 2.25\ SiO_2$$

The peculiar effect was produced when ware that came from the glost kiln with a bright green glaze was refired in a decorating kiln. The metallic film is supposed to be copper oxide.

The microscopic structure of the glaze is well described by Professor Orton as follows:

"I chipped off a sliver of the glaze, and put it on the field of a microscope of moderate power, and found that with its change from a bright smooth glaze to a dead metallic surface, the structure of the glaze had altered as profoundly as the color had. From a plane mirror-like expanse, it had become minutely ridged, resembling the ridges on the palm of the hand, but so fine that they cannot be seen clearly with an eight-power hand glass. There are millions of these little parallel lines, like waves and valleys."

Professor Orton seems to lean to the theory that this crinkled skin is due to an increase in volume of the material forming the skin. To our mind, this assumption is hardly necessary. We would not expect a layer of copper oxide to contract on cooling at the same rate as the underlying glaze. If the skin contracted while the glass was still plastic at a slower rate than the glaze, a crinkled effect, such as described, would be produced.

We classify this matte as belonging to the crinkled skin type.

SOME GENERAL OBSERVATIONS.

In none of the samples examined (unless we care to consider Matte XII as belonging to this class) did we find any evidence of the production of a matte by a scum of dry, undissolved, material floating on the surface of the glaze. In every case, both projecting nodules of undissolved matter and projecting crystals were coated with a thin film of glass. In fact, a consideration of the ordinary laws of surface tension, as applied to a layer of grains of solid material in contact with a layer of liquid, shows that the grains would, in all ordinary cases, be

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coated with the liquid. The presence of this lustrous surface on the particles is what makes the difference between a true matte and a dry slip.

In no case did we find any decided tendency for the coloring oxide used to go into any special part of the glaze structure. This observation applies particularly to copper-oxide, green mattes. In all the green mattes, two of which are known to be copper greens and all of which presumably are, the color was evenly distributed between glass and crystals, or glass and insoluble material, according to the type of matte. The copper oxide in green matte glazes may aid in some manner the production of matteness, but it certainly does not do so by a decided and uniform tendency to remain insoluble or to separate out in crystals.

CAUSE OF MATTENESS.

Matteness is essentially an optical phenomenon. Its occurrence depends upon the presence at the surface of the glaze of innumerable small lustrous surfaces set at a variety of angles. The light refracted from such a surface is diffused and gives to the glaze the soft velvety appearance so characteristic of a true matte.

CLASSIFICATION OF THE MATTES STUDIED.

This general type of texture may occur in several different arrangements and may be due to a variety of causes. Therefore, we have several types and sub-types of matte glazes. The twelve mattes we have described may be classified as follows:

I. The Crystalline Type.—In this type the matteness is due primarily to a crystalline structure on the surface of the glaze. We found it occurring in two forms:

(A) Large crystals with surfaces roughened by occluded matter. Specimen I, the Teco matte, is the only example found of this class.

(B) Small, clean-cut crystals. Specimen XI, the Hamilton matte, is the only example found of this class.

II. The Immature Glaze Type.—This term is one in accepted usage, but is not strictly accurate. All immature glazes do not give a matte surface, and other types of mattes may be due in

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part at least to immaturity. By the immature type of matte, we mean a glaze containing such a large percentage of undissolved material that the amount of glass present is not sufficient to cover the projecting portions but simply wets them with a thin film of glass. Many varieties of this type occur, depending upon the relative percentage of raw material and glass, the size of grain of the particles of raw material, and the manner in which they are distributed. In fact, no two mattes of this type are exactly alike. There is, however, a family resemblance in all of them, one example of which is the more or less evident water-marking found in all mattes of this type. In this type of matte, we found the following: Professor Orton's matte, the Van Briggle Art Co.'s matte, Brower's matte, the Grubey matte, Miss Cooke's copper matte, and the Rookwood red brown matte.

Inasmuch as this list contains the names of three beautiful and deservedly popular mattes on the market at the present time, the old canard, that an immature matte can not be beautiful or be made a commercial success, is shown to be ridiculous.

III. The Crinkled Skin Type.—This type of matte is due to the body of the glaze contracting more than a skin that has partially set. It might be due also to an expansion of the skin due to some phenomenon that would not affect the body of the glaze. There are probably several varieties of this type in existence. The two classes that we found are as follows:

(A) The Irregularly Crinkled Class.—In this, the forces causing the contraction seem to have been operative at different times. A possible case would be the elimination of bubbles of gas, for instance, CO_2, from the molten interior of the glaze. An example of this class is found in the Rookwood vellum matte.

(B) The Regularly Crinkled Class.—In this type, the contraction has taken place over the entire glaze at the same time and rate. An illustration of this would be the even cooling of a glaze with a high coefficient of contraction which is covered with a film of oxide with a lower coefficient of contraction. An example of this type is found in Jackson's black matte.

IV. The Gas Vesicle Type.—In this type, the matteness is due to the elevation of the skin of the glaze at innumerable points. There are in all probability several classes in this type,

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and this phenomenon is probably a slight contributory cause of matteness in examples classified under other types. We found at least some gas vesicles in all the mattes examined. The only example of this type of matte among those examined was Knollman's matte.

DISCUSSION.

Mr. Burt: At what were you looking, a cross section through the glaze or a section of the surface?

Prof. Staley: We examined the specimens both looking down upon their surfaces and in cross section.

Mr. Burt: Are you describing surface effects or the ultimate effect of the interior structure of the glaze on the production of matteness? I believe that some of our wares show a surface crystallization.

Prof. Staley: I found the crystals all through the glaze. The only glazes in which we found any appearance of surface crystallization were in the Teco matte and the Hamilton matte. In these, there was no real surface crystallization; the appearance was due simply to the fact that the glass had run away from the crystals. To the best of my knowledge, no crystal can grow out of the surface of a liquid unless it grows at one end only, which would be unusual. I have seen cases where it looked as if crystals had grown out of the surface of a liquid. I have always felt convinced that this appearance was due either to running away of the glass after the crystals had formed or to the fact that on cooling the glass had contracted more than a network of crystals and left them projecting from its surface. Of course the running away of the glass might consist of the glass simply soaking into the body. We can see that, if a surface of a crystal were projecting from a liquid, it would be impossible for the crystal to grow on this surface except by volatilization of material from the glass and the deposition of this material on the projecting crystal surface.

Mr. Burt: I understand the type you are speaking about, but it seems to me I remember Mr. Gates having a fringe of crystals reaching at least half an inch above the top of his vases.

Prof. Staley: They must have grown by volatilization.

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DISCUSSIONS WRITTEN AFTER READING THE PAPER.

Mr. Burt: Mr. Staley shows in his paper that the great majority of matte glazes in regular use seem to owe their matteness to "immaturity." With this I heartily agree. Practice shows that a highly crystalline glaze generally has the main body of the glaze receding as he says from the crystals, leaving them a confused mass generally rough with unoccupied cavities around them. These cavities fill at once with dirt, giving the glaze a surface impossible to clean. Hence we are driven to the so-called immature type as it gives a far better surface. While, therefore, I agree that in the main the affect is due to immaturity and that crystallization plays a minor part in these commercial mattes, I am surprised to find that his researches should show crystallization as almost non-existent. He says, for instance, of the Rookwood vellum "there has been a slight development of extremely small crystals," while a growth of small needles that I have always considered crystals can be seen with a hand glass if not with the naked eye. All makers of matte glazes realize how sensitive they are, how slight variations in heat treatment may produce the most varied results from the same glaze. Hence it is hardly conclusive to judge from a single sample of any glaze. My own examination with a hand glass shows crystals almost invariably present on the surface of regular mattes. In fact I have always considered this a ready means of telling a true matte from a refinished one. By "refinished" I mean a glaze which has come from the kiln a clear glaze and been sand-blasted or treated with acid for a matte surface.

The main point given us by this paper, to my mind, is that matteness is due to the unevenness of surface whether produced by immaturity, crystallization, or some other cause. This is undoubtedly true and is well illustrated in cutting glass. First, we have the clear glass piece into which is ground some design. In this state it is matte through uneven surface. Then, by most careful polishing, which is mere fine grinding to an absolutely even surface, we again have a clear glass. I see no reason why matte glazes could not be polished to full gloss.

Character and causes of this uneven surface then become a most interesting study. Mr. Staley considers crystallization, as

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said before, a very minor cause in most types of mattes. I can't help feeling, however, that crystallization may be of more importance than he would have us believe. Frost on a window gives all the gradation from a clear glaze to a full matte one, all due to crystallization. The same is true of crystal glazes. Let the crystal be in the plane of the glaze surface, and the glaze will be matte as are many of the true crystalline glazes. If the crystals are in a lower plane, we have high glaze with crystals seen beneath its surface as in the "Goldstone" glaze for instance, that is the "Aventurine." There is no need of the crystals growing out of the glaze surface as Mr. Staley says seems improbable to him but merely let them grow in the surface plane and their unevenness will give us a matte. To refer again to ice, we all know the beautiful frost crystals often a foot or two in size on windows; these I call a surface crystal producing matteness. Then we have clear ice enclosing snow. Here we have crystals below the surface not producing a matte surface. So while I agree that immaturity is the main cause of most matte glazes, I hold that crystals can and do play an important part at times.

Mr. Pence: We are fortunate in having the evidence of the microscope added to the other results of matte glaze study to be found in this volume. Petrographic examination is an important feature of such study and should be of especial interest in connection with the development of a theory for cause of matteness.

The foregoing paper is of interest as indicating the types of matte textures to be found in various fields of commercial usage, but is not sufficiently extensive or exhaustive to warrant general conclusions concerning the relation of composition and matte texture.

The results tend to confirm the theory that the barium matte is one of immaturity. With the exception of Glaze IX, the commercial mattes of immaturity examined very probably belong to the barium type. This is indicated by the descriptions given. It is of interest that of seven mattes in commercial usage examined, two were classified as crystalline.

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The crinkled surface matte is probably very rare and forms an exception to the regular matte types.

Further investigation may show that a surface composed of gas vesicles is characteristic of a family of fritted mattes of the types represented by Glaze X.

Two observations are given on matte glazes of the high CaO and Al_2O_3 type (Glazes VI and VIII). In both cases the matteness is assigned to immaturity due to the high percentage of undissolved material present. The description of Glaze VI shows that the result obtained in the glaze is abnormal. A glaze of the formula given when fired regularly at cone 1, should give a smooth matte with none of the alligator hide effect and glass rivulets as described. I consider the report on Glaze VI as having but little value as regards commercial glazes of this type. In the case of Glaze VIII, the composition is abnormal. The Al_2O_3 is very much higher than we would expect to find in this type of glaze, 0.35 Al_2O_3 being normal. Also, the SiO_2 is low. Glaze VIII might be expected to show immaturity. However, a rather high percentage of glass is found and some crystals occur.

We must remember also that these glazes were very probably subjected to a firing and cooling treatment of considerably shorter duration than that of commercial practice.

While the observations on Glazes VI and VIII indicate to a small degree that glazes of the type

$$\left.\begin{matrix} 0.55\ PbO \\ 0.15\ KNaO \\ 0.30\ CaO \end{matrix}\right\} 0.35\ Al_2O_3,\ 1.55\ SiO_2$$

owe their matteness to immaturity, the evidence at hand is entirely inadequate to confirm this theory. Further microscopic study of such glazes of normal composition and treatment may show immaturity to be the cause of their matteness. My own observations of the working of such glazes in the factory does not support such a view.

Mr. Purdy: Mr. Pence has repeatedly referred to the kind of work we can do in our small kilns. Now I know what factory results are and I know the limitations of small kilns. I therefore state, with considerable assurance of being correct, that in our coke-fired kilns, in which we take the same heating and cooling

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curve as obtained in factory kilns, we can duplicate very closely to factory conditions. I most strongly protest against the imputation Mr. Pence implies when he refers to our experimental kilns that will hold 12 saggers, 18″ x 8″ x 8″.

Professor Staley I am well satisfied with Mr. Burt's discussion; his final conclusion agrees well with the evidence I have brought forward. In regard to what Mr. Pence has said, I wish to add a few remarks.

He says that the investigation is not sufficiently exhaustive to warrant general conclusions concerning the relation of composition and matte texture. I have not attempted to do so; but inasmuch as this is the first paper giving direct evidence on the micro-structure of matte glazes, it is certainly deserving of some consideration.

Whether a glaze of composition similar to VI gives a smooth matte or one with an alligator hide effect, when fired at cone 1, depends largely on the thickness of dip. The particular example examined happened to be dipped quite thick and was chosen because we wanted to study a glaze with this particular effect. We had on hand at the time quite a variety of samples of similar compositions (some fifty different compositions), all with a similar matte texture but grading down from the alligator hide effect to a smooth matte. A cursory examination of several of these under the microscope was sufficient to convince us that the micro-structure was essentially the same in all the gradations.

I am not aware that there is any compulsion for a calcium-alumina matte to confirm to any particular formulae. I have seen mattes of this type made over a rather wide variety of formulae. Therefore, I am at a loss to understand what Mr. Pence means by saying that glaze VIII is not normal—unless he means that it does not conform to the formula he has been using. However, to meet him on his own ground, I will say that I have before me, as I write, a glaze trial of the same RO as VIII but with an alumina and silica content very nearly "normal," 0.30 Al_2O_3 and 1.60 SiO_2. The general appearance of this trial varies somewhat from VIII, there being a small bright patch at one end. Microscopic examination shows that the internal structure of the

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matte portion is qualitatively the same as that of VIII, but that quantitatively there is present less of the undissolved matter. This was to be expected from the difference in the batch.

Finally, Mr. Pence says that his observations on the working of calcium-alumina mattes in the factory does not support the view that the matteness is due to immaturity. This may be true, although he, or any one else, has published no observations that would even tend to show that raw calcium-alumina mattes are not due to immaturity of a certain type, consisting of the presence of a glassy matrix and considerable undissolved matter. What these compositions do when fritted has no bearing on their action raw. Nor, on the other hand, could the factory experience of Mr. Pence, or of any one else, be expected to give much support to any opposing view.

The glaze structure that gives a true matte texture is microscopic, is far beyond the powers of observation of the human eye, even when aided by a hand glass. Evidence on this question drawn from factory experience must always be inferential and subject to rebuttal by the first direct evidence that can be brought to bear on the subject. All of us have the most profound respect for practical experience in its proper fields. Factory experience can teach us many valuable things about matte glazes, how to compound them, how to dip them, how to burn them; but in regard to the physical basis of the matte texture, it can teach us practically nothing. This is a case where seeing is believing, and the only way you can *see* the micro-structure of a matte glaze is by looking at it through a powerful microscope with the eye of an experienced observer.

The results of this investigation were as much a surprise to me as to any one else, for I too thought that most mattes were crystalline; but if we are to be at all open-minded, neither I nor any one else can refuse to accept the evidence at its true value.

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THE DEHYDRATION OF CLAYS.[1]

By G. H. BROWN AND E. T. MONTGOMERY.

Considering the economic importance of clays, little investigative work has been done as to their decomposition and other points indicated by loss of water, heat absorption and evolution, and specific gravity changes. Le Chatelier[2] divided clays into five groups on the basis of retardations and accelerations in the heating curve. His temperatures have been proven too high. Bleininger[3] preheated clays at temperatures below 400° C. and found a marked decrease in plasticity and improved working qualities where desired. Orton[4] in seeking to improve certain sticky clays failed to get results at the lower temperatures and was compelled to resort to higher. The work of Mellor and Holdcrof[5] on the "Chemical Constitution of the Kaolinite Molecule" has thrown much light upon the subject. The recently published articles of Rieke[6] has covered considerable of the field as to the losses in weight when heated to different temperatures and the rate at which the water of hydration is given off. The present investigation was undertaken under the following heads:

1. The heat absorption of clays.

2. The loss in weight of clays when heated at constant temperatures.

3. The loss in plasticity of clays due to heating to constant weight at different temperatures.

For the investigation the following clays were selected:

1. North Carolina kaolin.
2. Georgia kaolin.
3. Tennessee No. 3 ball clay.
4. A No. 2 fire clay.
5. A refractory plastic fire clay.
6. Flint clay.
7. Shale.
8. Shale.
9 Highly plastic surface clay.
10 Highly plastic surface clay.

An-air dried sample of each clay was passed through a 20-mesh sieve, tempered, and thoroughly wedged on a plaster block.

[1] By permission of the Director of the Bureau of Standards.
[2] Z. physik. Chemie, I, 396 J Ind. and E. Chem. III, 2, 91.
[3] A. C. S., XII.
[4] A. C. S., XIII.
[5] T. E. C. S., X, 94–120
[6] Sprechsaal, 44–45.

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Enough from each sample was prepared to allow the cutting of all samples from the same lump.

PART I.

THE HEAT ABSORPTION OF CLAYS.

For the heat absorption work cylinders $3^3/_8''$ in length, $1^7/_8''$ in diameter, and having a $^7/_8''$ hole cut through the center, were prepared.

An electric furnace wound with nichrome wire and having a heating chamber 2″ in diameter x 5″ in length was used. The furnace temperatures were measured by a platinum-platinum rhodium thermocouple and millivoltmeter, the junction of the couple being placed outside of the piece. The cold junctions of the couple were immersed in an ice bath. The bulb of a resistance pyrometer was inserted through the center of the piece and used for recording the inside temperatures. The temperature of the furnace was increased at a uniform rate by means of a regulating rheostat. The temperatures inside the test piece were recorded at intervals.

The test pieces were dried at 110° C. until constant in weight and at 200° C. before inserting into the furnace. In Fig. 1 are seen the temperature retardations of the different clays.

The rate of heating of the furnace is shown by the straight line at the top.

Taking up the clays in order the observations were as follows:

1. North Carolina kaolin. This clay shows a marked retardation, first distinguished at about 480° C., the main heat absorption being between 540° and 570°. The loss in weight of the clay at 650° was 13.20 per cent.

2. Georgia kaolin. This shows a heat absorption beginning at 525° and most pronounced between 520° and 590°. The loss in weight of this clay was 12.93 per cent. at 650°. The curve appears drawn out over a longer interval than that of the North Carolina kaolin.

3. Tennessee No. 3 ball clay has a retardation beginning at 500° and greatest between 520° and 590°. The loss in weight was

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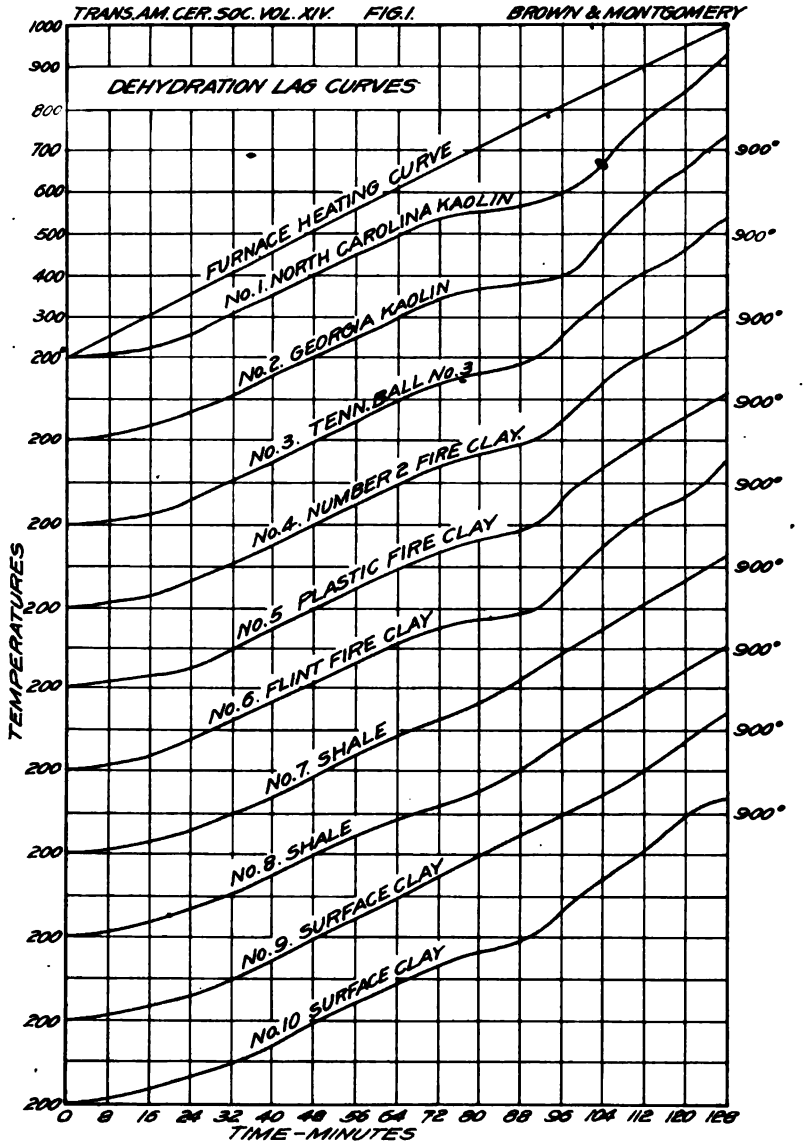

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10.67 per cent. at 650°. The retardation was less pronounced than that of the two kaolins.

4. The No. 2 fire clay shows a lag beginning at 475° and greatest between 570° and 605°. The loss in weight at 650° C. was 6.69 per cent. The retardation shown by this clay is less than that of the three preceding clays.

5. Plastic fire clay. The first drop in temperature is at 475°, the main heat absorption lying between 550° and 580°. The loss in weight was 5.68 per cent. The lag is more pronounced than that of the No. 2 fire clay.

6. Flint fire clay. This clay shows a decided retardation, first visible at 475° and more pronounced between 540° and 560°. The loss in weight was 10.45 per cent. at 650°. The retardation shown by the flint clay is similar to that of the kaolins.

7. A shale shows a slight retardation first visible at 485°. The loss in weight was 3.98 per cent. at 650°.

8. A shale has a very indistinct lag. The loss in weight was 4.88 per cent. at 650°.

9. A highly plastic surface clay shows no heat absorption. The loss in weight was 5.63 per cent.

10. A highly plastic surface clay shows only a slight lag first visible at 490°. The loss in weight was 10.09 per cent.

DISCUSSION OF RESULTS.

For the majority of the clays the first retardation was noticed between 475° and 500° C., the greatest heat absorption lying between 540° and 600°. The purer clays show the bulk of the water given off between 540° and 560° C., the two kaolins and the flint clay having the most decided lags. These three clays show the highest water content. The size of the lag, however, is not a criterion of the amount of water present in the impure clays. Surface clay No. 10, which shows a loss in weight of 10.09 per cent., has only a slight retardation, while clay No. 5 has a decided lag yet has a loss in weight of 5.68 per cent. The loss in weight of the impure clays is partly due to oxidation and probably other reactions to some extent, and is not strictly comparable to that of the kaolins and flint clays.

As will be shown later the temperature at which a retarda-

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tion is first visible is not the temperature at which the water is first given off. The initial retardation is governed more or less by the manner in which the furnace is manipulated, the size and condition of the clay sample used, and the rapidity of heating. Thus, when the furnace was heated in one-half the time used, a smaller lag was secured and a retardation was first noted at a higher temperature. By increasing the time the lag was less pronounced.

PART II.

THE LOSS IN WEIGHT OF CLAYS WHEN HEATED AT CONSTANT TEMPERATURES.

The same clays were used for this part of the investigation, a small cylinder 1″ long and $^3/_8$″ in diameter and weighing about 10 grams having been adopted as a test piece. The same type of furnace was used, the test piece being placed in the zone of most equal heat distribution. The temperatures were measured by the use of thermocouple and millivoltmeters. Also a potentiometer indicator was used for checking the instruments.

Each piece was dried at 110° C. until constant in weight. The temperatures of heating were 200°, 400°, 450°, 500°, 550°, 600°, 650°, and 700° C. The fluctuations were not more than 5° C. in either direction. The accuracy of the temperature measurements were those of the couples and instruments used.

The pieces were heated until the loss in weight was 0.2 of 1 per cent. after a two-hour heating period. In Fig. 2 are shown the losses in weight of 7 clays, the other four being omitted on account of overlapping.

The losses in weight at 200° were small, varying from 0.10 of 1 per cent. to 1.4 per cent. The pieces were heated to constant weight without difficulty.

The losses at 400° were greater, especially with surface clays 9 and 10, which lost 2.83 per cent. and 3.13 per cent., respectively.

At 450° C., a gradual loss was secured by continued heating, the amounts driven off decreasing as the time of heating increased. The removal of the last traces of water was found impracticable. The North Carolina kaolin lost 11.5 per cent. of

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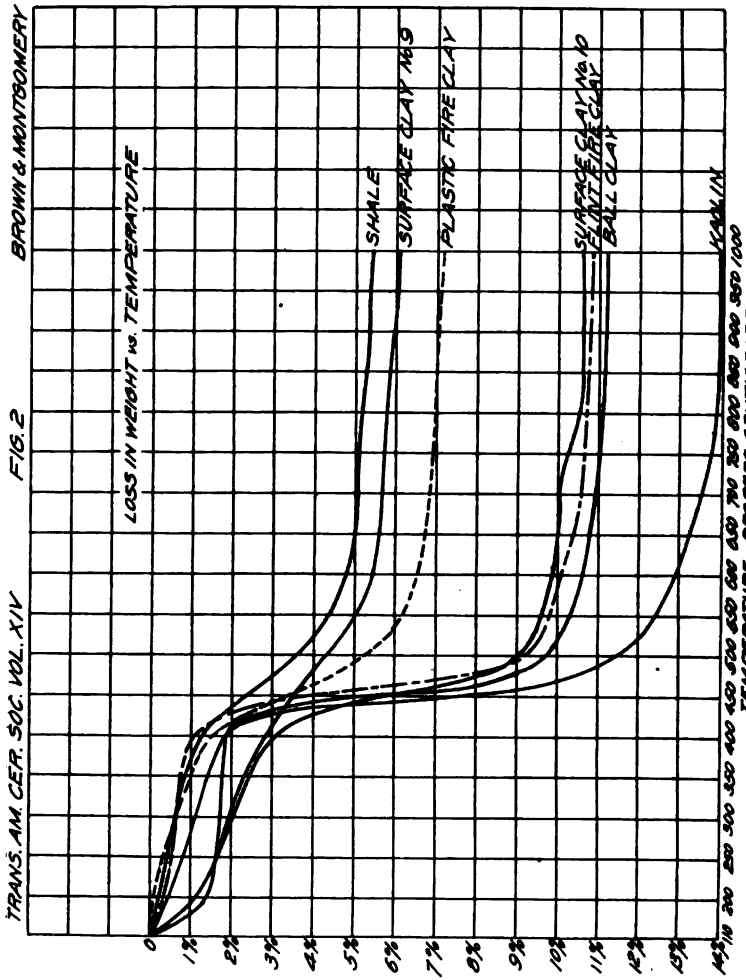

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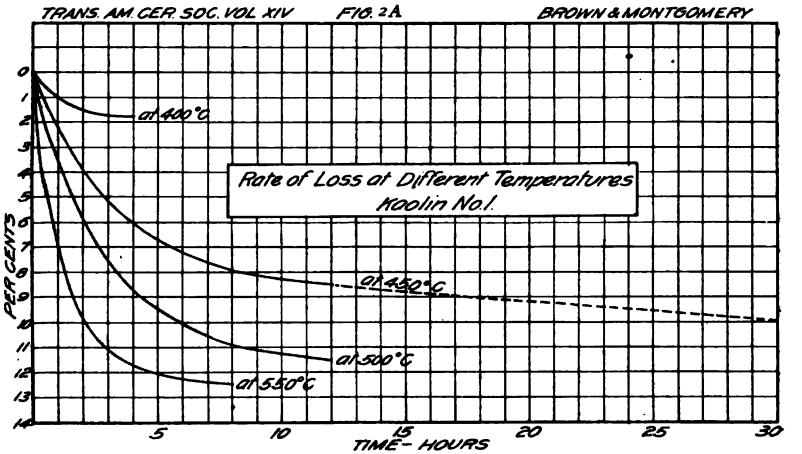
water at the end of $57^1/_2$ hours' heating at 450°. The Georgia kaolin lost 8.3 per cent. by weight at the end of 36 hours' heating. It is evident that by a sufficient length of heating period, the entire water content could be driven off at 450° C. At 500° the rapidity at which the water could be driven off increased. The last traces, however, were still held tenaciously. At the higher temperatures only traces of water remained, the amount decreasing with increase in temperature (see Fig. 2A).



DISCUSSION OF RESULTS.

The two surface clays and the ball clay lost more in weight below 450° than did the other clays. These surface clays have been subjected to the preheating treatment on samples of 300 pounds in size, and have been found to lose a great part of their plasticity. In tests described later on, the ball clay was found to have a considerable loss in plasticity when heated to 400° C.

The slope of the curve of surface clay No. 9 is somewhat gentle and does not show a drop at 450°. It will be noted from Fig. 1 that this clay had no retardation in its heating curve. The same is true also for the shales which show only slight retardation in their heating curve, and a somewhat gradual loss in weight with increase in temperature.

In the case of the shales and surface clay No. 9, the lack of

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retardation and the gradual expulsion of the water with increase of temperature indicate the presence of various compounds which liberate their water at different temperatures.

At this point attention is called to the work of W. M. Kennedy,[7] a former pupil of Orton's. He shows a loss in weight versus temperature curve, secured by heating a 30-gram sample of Florida kaolin over a period of 28 hours. His curve is very similar to that secured on the kaolins used in this investigation.

PART III.

THE LOSS IN PLASTICITY DUE TO HEATING TO CONSTANT WEIGHT AT DIFFERENT TEMPERATURES.

A 60-gram test piece was adopted for this work, the heating being in the same type of furnace used for the other work. The pieces were dried at 110° until constant in weight, and then heated until practically constant in weight at 350°, 400°, 450°, 500°, 600°, and higher when necessary. After heating, the pieces were ground in a mortar, passed through a 20-mesh sieve and tempered and molded into cylinders. Enough water was added to give good molding qualities. The plasticity and working qualities were noted by personal observation. The wet piece was allowed to remain in a desiccator over water for 3 hours, and the wet volume determined in a small volumeter, using kerosene. After drying to constant weight at 110°, the pieces were paraffined and the dry volumes measured.

DISCUSSION OF RESULTS.

The working qualities of the clays were observed as follows:

No. 1 North Carolina Kaolin.—After preheating to 110° the plasticity was the same as that of the air-dried sample.

After preheating at 350°, a slight decrease in plasticity was observed.

The plasticity at 400° was the same as that at 350°.

The sample preheated to 450° showed a large decrease in plasticity, the clay being granular in character. At 500°, 550°, and 600°, the granular structure increased.

No. 2 Georgia Kaolin.—Preheating at 110° caused a slight

[7] Trans. A. C. S., IV, p. 146

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decrease in plasticity. A quite noticeable decrease occurred after preheating at 350° C.

At 400°, there was a slight decrease over that at 350°.

At 450°, a large decrease took place, and the granular structure was again developed, as with the North Carolina kaolin at the same temperature.

At 650° and 700°, there is no further change. A large loss in plasticity is caused by heating at 750°, and at 800° the plasticity is entirely destroyed.

No. 6 Flint Clay.—The initial plasticity of the flint clay was small and decreased slightly with each increase in the heating temperature. The test pieces could not be molded after heating at 600°.

No. 7 Shale.—An air-dried sample of this clay had about the same plasticity as most shales.

There was not a noticeable decrease at 110°. At 350°, there appeared to be a slight increase in plasticity. This was observed by the improved working and molding properties.

At 400°, it may be said there was a further slight increase.

At 450°, the behavior was the same as at 400°. At 500° and 550°, there was no change in behavior over that at 400° and 450°.

A very slight decrease in plasticity was observed at 600°.

At 650° and 700°, the clay undergoes but slight change. A large decrease in plasticity occurs at 750° and the working properties are destroyed.

No. 8 Shale.—The behavior of this shale is very similar to that of shale No. 7, the plasticity being retained without decreases when heated at temperatures below 650°.

No. 3 Tennessee No. 3 Ball Clay.—This clay appeared to have a slight decrease in plasticity at 110° over that of the air-dried sample. At 350°, a decided decrease was observed, the clay being no longer sticky but having the working qualities of a No. 2 fire clay.

At 400° there was a further large decrease, the clay assuming the granular structure observed in the two kaolins when heated to 450°.

Preheating at 450° developed a sand structure.

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No. 4 No. 2 Fire Clay.—The plasticity of the No. 2 fire clay was not materially decreased when heated to temperatures below 450°. At this temperature there is a large decrease in plasticity, although this clay still has fair working properties.

At 500°, a further slight decrease in plasticity is noted. At 550°, there is no noticeable change over that at 500°.

A somewhat granular structure is developed by heating at 600°.

No. 5 Refractory Plastic Clay.—Only a small decrease in plasticity is noted upon heating to 350°.

At 400° and 450°, there is no further decrease in plasticity over that at 350°. Although the clay appears slightly granular when water is first added, the plasticity is rapidly developed.

At 500°, the plasticity is apparently the same as at 450°; and at 550°, only a slight decrease is observed.

Heating to 600° causes a quite noticeable decrease, although the clay is still quite plastic.

At 650°, a slight decrease in plasticity is observed over that of the air-dried sample. At 700°, there is a further decrease; and at 750°, the clay loses its ability to be noted.

No. 9 Surface Clay.—This clay is exceedingly sticky and is dried with difficulty.

When preheated at 110°, no noticeable change in plasticity occurs.

At 250°, the clay loses its stickiness and has improved working properties.

At 300°, there is a further reduction in plasticity.

At 350°, the plasticity is practically destroyed, the structure becoming granular.

Preheating to 400° and temperatures above causes no further changes.

No. 10 Surface Clay.—This clay also is of the sticky variety, being similar to the so-called joint clays. No reduction in plasticity is caused by heating to 110°.

At 250°, the stickiness disappears and the working properties are improved.

A further decrease in plasticity occurs at 300°.

Preheating at 350° develops a granular structure with poor

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working properties. At 400° and higher temperatures, the plasticity is destroyed.

VOLUME SHRINKAGES.

The percentage volume shrinkages of the clays at the different temperatures are shown in Fig. 3.

The North Carolina kaolin shows a volume shrinkage decreasing rapidly when 450° C. is reached.

The volume shrinkage curve of the Georgia kaolin is somewhat similar to that of the North Carolina kaolin, being greater, however, at the higher temperatures.

The volume shrinkage of the Tennessee ball clay decreases rapidly as the temperature increases. Preheating this clay at temperatures below 450° caused large reductions in plasticity.

The volume shrinkage curves of the No. 2 fire clay and the plastic fire clay are somewhat similar, at the lower temperatures. The effects of preheating the two fire clays were not the same, the former losing considerable of its plasticity at 450° while the latter was not materially affected at temperatures below 600°.

The two shales show changes in volume shrinkages which are similar.

The plastic surface clays show rapidly decreasing volume shrinkages with increase of preheating temperatures.

In most cases, the volume shrinkages of the clays are in accordance with the personal observations made as to the plasticities. The kaolins showed a large decrease in plasticity at 450°. The ball clay and the two surface clays showed marked decrease in plasticity when preheated at the lower temperatures. The fact that shales do not lose their plasticity at a red heat has been noted by Purdy,[8] who records that after heating a shale from 500° to 800° for 17 hours, it slaked down to a red plastic mass in water.

The per cent. water added in tempering the clays after preheating are plotted against the different temperatures in Fig. 4. At the higher temperatures the loss in plasticity is usually accompanied by an increased amount of water required for working.

[8] I. S. G. S., Bull. 9, 185.

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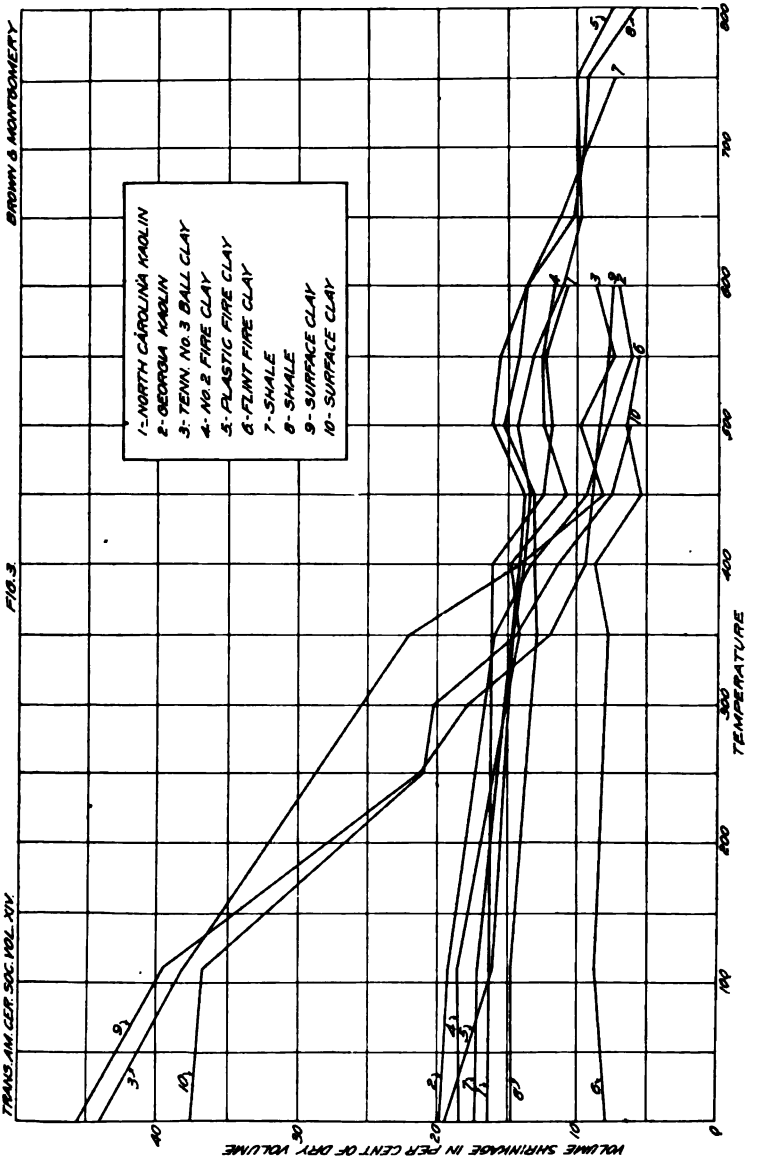

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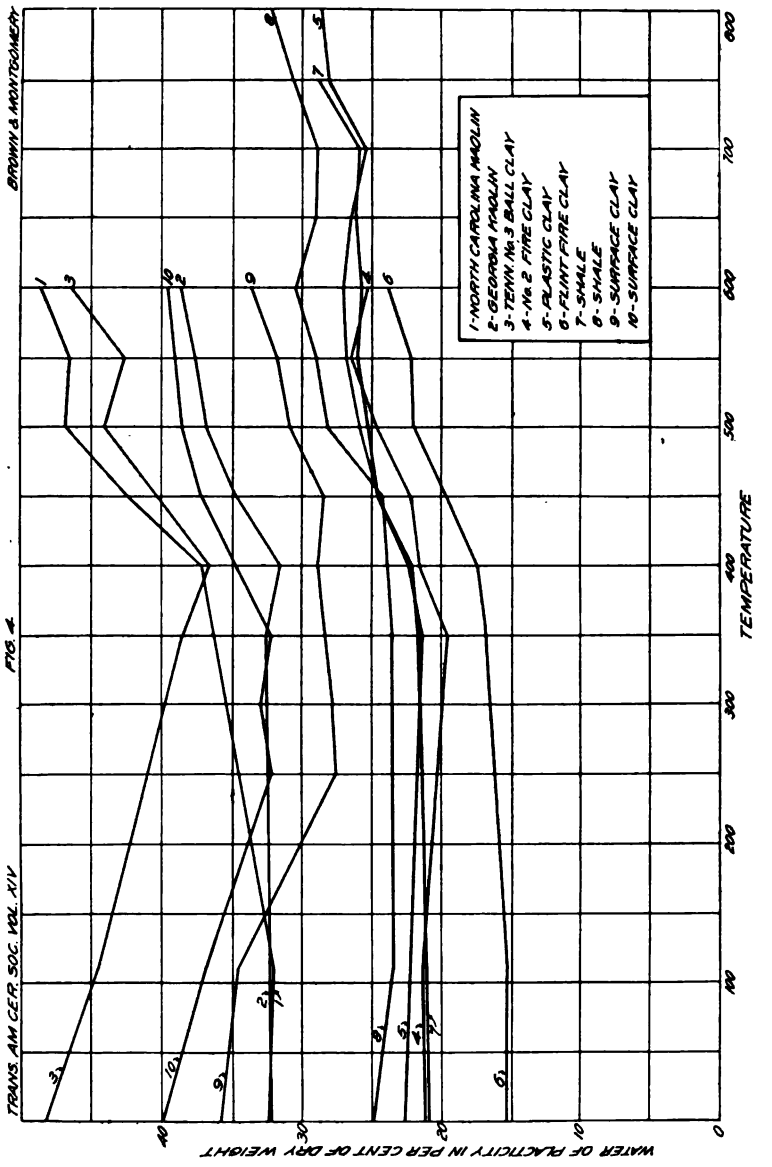

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SUMMARY OF RESULTS.

In Part III of the investigation, we find clays which lose their plasticity at temperatures below 450° C., others which lose their plasticity upon being preheated at 450°, and still others which are only materially affected at temperatures as high as 750° C. The possible loss in plasticity of a clay when preheated to temperatures below 450° seems to be partly governed by the amount of water given off at those temperatures. This was found true for the ball clay and the two surface clays. In almost every case where there was a loss in plasticity, a granular structure seemed to have developed. In other words, the preheating, aided by the presence of some cementing material, caused an agglomeration of the particles. In some cases these granules were broken down as soon as water was added.

This cementing did not take place in the shales nor in the plastic fire clay, and may possibly be due to the different character of the colloidal portion of the clay. The air-dried samples of the shales and of the plastic fire clay were soft and easily crushed, as were the samples preheated at the temperatures below which plasticity was not destroyed. The ball clay and the surface clays were crushed with some difficulty after the preheating treatment.

CONCLUSIONS.

The results of the investigation confirm the observations of Rieke as to the temperatures and rates of dissociation for typical clays. Rieke's statement that the loss of plasticity does not appear to be closely connected with the loss of combined water is borne out by the behavior of the clays tested.

The work of both Bleininger and Orton as to the effect of preheating is substantiated as to temperatures. Clays occur which if preheated below 450° lose their plasticities. Other clays occur which do not lose their plasticities at the dehydration temperatures or temperatures much higher. Where preheating causes loss of plasticity, the amount of this loss is a function of the time of heating as well as of the temperature.

Acknowledgment is made to Prof. A. V. Bleininger for the outline and helpful suggestions as to the carrying out of the work, and to Mr. Paul Teetor, who assisted in the laboratory experiments.

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PHILIPPINE POTTERY.

By C. H. CROWE, Philippine School of Arts and Trades, Manila, P. I.

The purpose of this article is to give a brief history of Philippine pottery and to show what is being done to develop the clay working industry.

Much primitive, crude, red pottery is made throughout the Philippines. The value of this is roughly estimated at $200,000 a year. The products are mostly pots for cooking or holding water. None are glazed. Some are decorated with lines scratched with a stick on the unburned clay.

The clay used is generally sedimentary and always unrefined. Water is mixed with the clay and the mixture is tramped with the bare feet, care being taken to pick out the sticks and stones. As the clay often shows a great air shrinkage, fine river sand is sometimes mixed with it.

The clay is roughly made into cup shape articles and then set away to dry to a tough, leathery consistency. These are then given a second shaping by holding a smooth stone inside and beating them with a wooden paddle. The beating renders the clay more compact and tends to prevent cracking while drying. Sometimes to make the surface more smooth, the objects are painted with a fine grained, red slip (probably ochre) and then polished with a piece of a large shell. When the pots are dry, they are piled on a layer of bamboo sticks and rice straw, covered with more of the same fuel, and burned in the open. The firing is completed in a few minutes.

This manufacturing of pottery is carried on as a household industry. The pots are usually made by the women and children while the men get the raw material and market the product. Passing through the towns or *barrios* that are the centers of the pottery industry, one sees the pots piled for sale in nearly every yard and hears the beating of the paddles from every house as the pots are being formed.

There are but few kilns in the Philippine Islands. The Spanish introduced the dome-shaped beehive kilns which were used to fire the Spanish roofing tiles so much employed before

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Fig. 1.—1, Shaping; 2, Beating; 3, Polishing pilones.

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Fig. II.—1, Burning in the open; 2, Method of transporting; 3, Marketing.

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corrugated roofing iron was imported. This type of kiln is now used for firing brick. The usual type of pottery kiln is a long, semi-cylindrical structure introduced by the Chinese. In these kilns are produced the large *tenajas* (jars for carrying water, vinegar, cocoanut oil, nipa sap, etc.) and sugar *pilones*. The kilns are fired with wood, and the temperature attained is low, but the clay is very fusible and a semi-vitrified ware results. A Japanese kiln has lately been introduced. This consists of two ovens, the first for glazing and the second for biscuit-burning. Three of these kilns are now being operated in the Philippines.

The Bureau of Education recognized the needs of the Filipinos, and, in accordance with its industrial policy, organized a pottery school in 1910. This school was started in Laguna Province but was later moved to Manila and became the Ceramic Department of the Philippine School of Arts and Trades.

The students of the wood-working course constructed the building for this department and the following equipment was made in the school: a blunger of 40-gallon capacity, a settling tank of 120-barrel capacity, one kiln 12 feet by 24 feet (containing two ovens), one small test kiln, eleven potters' wheels, a kneading table, a modeling table, drying racks, and a filing case for clay samples and tests. The equipment includes the following power machines: a cup machine, a saucer and plate machine, a lathe, a ball grinder, a glaze mill and a polisher. This equipment accommodates 60 pupils and with it, terra cotta, faience, stoneware, porcelain, and all other classes of clay products can be made.

The Ceramic Department aims to train boys so that they will be able to equip and operate a factory. In this first year of the course, the students have constructed the kilns, made tiles, common bricks, fire bricks, and common glazed ware (faience) of various colors and designs.

Sixteen provinces have submitted samples of clays, and on them 100 tests have been made. Fifteen samples of grayish and white so-called *yeso* have been received. Of these, seven burned a white color, six gray, one red, and two buff. Clays from Los Banos, Laguna, and from Nasugbu, Batangas, have been received in bulk and have been used separately, mixed together and mixed with common clay, in each case with good salable

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Fig. III.—Students at work in the Ceramic Department, Philippine School of Arts and Trades.

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Fig. IV—Refractory ware and terra cotta made by students of the Ceramic Department of Philippine School of Arts and Trades.

Fig. V.—Faience made in factory owned and operated by two boys who had one year's training in Ceramics.

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TABLE OF MECHANICAL TESTS OF CLAYS.

Clays.	Shrinkage.		Color.		Cone.	Remarks.
	Air.	Fire.	Air.	Fire.		
Salsona, Ilocos Norte	11%	1%	White	White	4	With proper handling will make good stoneware or porcelain.
Sta. Cruz, Zambales	5	3	White	White	4	
Nasugbu, Batangas	3	1	White	Grayish	6	
Los Banos, Laguna	6	8	White	White	6	
2/3 Los Banos, Laguna	10	10	Gray	Dark red	6	Well vitrified.
1/3 San Pedro, Metaci						Kept their shapes.
Liloan, Cebu	8	3	Brown	Dark red	6	
1/2 Los Banos, Laguna						
1/2 Nasugbu, Batangas	4	8	Whitish	Gray	6	Very refractory.
1/2 Los Banos, Laguna (white rock like)						
1/2 Sta. Cruz, Zambales	4	1	Whitish	Gray	6	

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results. Further experiments with the white burning clays will be made for stoneware and porcelain.

Twenty-nine clays and mixtures have been tested for vitrified brick. Of these, three warped slightly, five cracked, one swelled, fifteen showed too short a range between vitrification and viscosity, and five with a slight variation of mixture would apparently make a good commercial brick.

The most successful experiments were those on refractory ware. Fire bricks, fire clay tiles and posts have been made and used in the kilns and have in every way served as well as the imported product.

Only mechanical tests are made but these show shrinkage, color, hardness, warping, cracking, etc., from which the usefulness of a clay can be determined. Some of the results of these experiments are found in the preceding table.

After studying for nine months in 1910, two boys have been able to organize a small factory and are now earning their living. They made their own bricks and built the kiln. They refine the clay, prepare the glazes, and do all the work. They make glazed and unglazed flower pots, water jars, pitchers, water coolers, trays, toys, etc. This makes a decisive step in the advancement of clay work, as heretofore no Filippino has refined a clay or has been able to make a glaze. It is also indicative of what may be expected from the teaching of clay work in the Ceramic Department. The forty students who are now studying ceramics will later go to their various provinces to make use of their knowledge in pottery schools or in factories. In this way the knowledge of clay work will be spread throughout the islands.

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*Analyses of typical Philippine clays are given.—Editor.

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THE CHEMICAL ROLE OF BORON IN GLAZES.[1]

By Ross C. Purdy, Columbus, O.

I question the validity of the arguments that have heretofore been put forward for considering B_2O_3 as functioning the same as Al_2O_3. I do not want it taken that I am criticizing the placing of B_2O_3 with Al_2O_3 in the empirical molecular glaze formula, for these formulae are merely mechanical ways of expressing a convenient grouping of the oxides, and if it is convenient to write B_2O_3 with the Al_2O_3, that is sufficient argument for so doing. I want, however, to question the claims that have been advanced as proofs of the similarity in function of Al_2O_3 and B_2O_3.

Professor Binns says in the discussion of paper by Bleininger (this volume) on "Thermal Studies of SiO_2-B_2O_3 Mixtures" that he has been confirmed by Dr. Singer and Professor Stull and has no reason for retreating from the position he took concerning the rôle of boron in glazes. His original arguments were as follows:[2]

(1) "Analogy." "So far as we are aware all of the sesquioxides exert both acid and basic functions."

(2) "Reactions." "It has been shown that upon the melting of silica and boron sesquioxides together, heat is evolved....."

(3) "Practice." "Glazes containing boron sesquioxide do not obey the bisilicate law if boron be regarded as acidic, but this law is immediately obeyed if the boron be regarded as basic."

A. I do not deny the partial truth in his analogy argument. I can say, however, as I have said before,[3] "I know there are boron phosphates, and I know that all attempts to show that boron is a base have, as a rule, failed; and that the boron phosphates, boron chlorides, etc., are rather unstable compounds. In environments to be found in a fused glaze, boron might possibly be combined with an acid, as for instance, forming a boron silicate."

I have yet to see proof that boron functions as a base in stable compounds, igneous or otherwise. This argument by

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[1] Contribution from the Ceramic Engineering Laboratories of the Ohio State University.

[2] Trans. A C. S., Vol. X, p. 167.

[3] Trans. A. C. S., Vol. X, p. 171.

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analogy is based on very weak circumstantial evidence, in fact is almost wholly without proof. It can not be given much credence.

B. Professor Bleininger has shown that Binns' argument on "Reactions" was based on malreadings and hence need not be further considered.

C. Professor Binns' "Practice" argument deserves consideration and does not need to be substantiated, so far as the construction of the empirical molecular formula is concerned, by any proof other than that of convenience in manipulation and reading of the empirical molecular formulae. But do fritted glazes follow the "bisilicate law?"

In Volume IX of our Transactions, page 97, I quote five fritted glazes. In these, with B_2O_3 considered as a base, we would have oxygen ratios of 1.87, 1.5, 1.76, 1.78, 1.38, respectively.

A study of the curves on pages 157–171 of Volume IX of our Transactions makes plain that in all groups, the glazes of Series 1 to 5 (those highest in B_2O_3) had the longest heat range; and the data shows that they were freest from crazing. The oxygen ratio of these glazes, with B_2O_3 considered a base, would be as follows:

	GROUPS.				
Series.	1.	2.	3.	4.	5.
1.....	0.94	1.08	1.20	1.30	1.35
2.....	1.05	1.22	1.36	1.49	1.54
3.....	1.13	1.32	1.48	1.63	1.69
4.....	1.26	1.49	1.68	1.86	1.95
5.....	1.42	1.70	1.95	2.18	2.28

It should be noted that the groups increased progressively in oxygen ratio, that the series decreased progressively in B_2O_3 content, and that the above values hold true in the glazes for all contents of Al_2O_3. Further increase in oxygen ratio or decrease in B_2O_3 resulted in decreased excellency in every respect, hence such glazes are considered impractical.

These examples go to show that Binns' "Practice" argument is without foundation. He cannot hold his position longer on this line of reasoning, unless he presents proof in support of his

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argument. This he never did, although he has claimed to now have no more trouble in formulating fritted glazes than he has in raw glazes, both obeying the same law.[4] In the glazes he cited, according to his own admission, "*the faults of the glazes are more eloquent than their excellences.*" His glazes certainly were not eloquent in support of his contention for none were anywhere near perfect. In fact, no one would attempt to compound glazes the like of those he used as illustrations, so irrationally were they proportioned.

Aside from the imperfections of all his glazes pleading eloquently against his claims, one of his series speaks especially eloquently for a difference in the role played by the two R_2O_3. A study of Seger,[5] "Note on Glazes Free from Lead," makes plain that in the type of glaze with which he was experimenting, and which are similar to those in Professor Binns' Series V, the Al_2O_3 must be increased as the B_2O_3 is increased to avoid the very troubles which Professor Binns reported but of which he said "these glazes present the appearance which is usually attributed to an excess of alumina." Experience in our own laboratory checks that reported by Seger, hence we must conclude that in this series, Binns should have increased the Al_2O_3 to counteract the effects of the B_2O_3. Does this show that these two R_2O_3 oxides play the same rôle? Quite the contrary.

I have shown that so far as any evidence Professor Binns has presented, there is none in support of the contention that, in glazes, B_2O_3 plays the same rôle as Al_2O_3. I will now review the evidence presented by Dr. Singer[6] and Professor Stull.[7]

Dr. Singer, in his introductory remarks, misquotes Purdy and Fox when he says that "they conclude that the radicals B_2O_3 and Al_2O_3 are analogous in glazes." He also quotes Binns to the same effect. I have just proven that the latter quotation could not support the claims that B_2O_3 and Al_2O_3 function alike in glazes, and in the discussion of Dr. Singer's paper, I have already called attention to the points in which he erred when

[4] Trans. A. C. S., Vol. XII, p. 140.
[5] Seger's "Collected Writings," Vol. I, p. 453.
[6] Trans. A. C. S., Vol. XII, p. 676.
[7] Trans. A. C. S., Vol. XII, p. 129.

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quoting Fox and myself. The evidence presented by Fox and myself would certainly show that B_2O_3 and Al_2O_3 did *not* function alike. The further citations by Dr. Singer are admittedly in proof that B_2O_3 and Al_2O_3 function alike when as acids and not as bases. Binns contended that they functioned alike as bases.

Dr. Singer made what he called a "Replacement of Al_2O_3 by B_2O_3 in unfritted matte glazes, claiming that in this the B_2O_3 and Al_2O_3 appeared to function alike. Stull, discussing this series, very aptly drew attention to the fact that these glazes were admittedly (by Singer) immature mattes and that the substitution of calcium borate for clay simply reduced the maturing temperatures.

Furthermore, Dr. Singer attaches significance to the oxygen ratio of 2 for a cone 7 matte glaze, using two cases in illustration. Professor Orton adequately states the want of significance in this ratio, and Dr. Singer's own series, whether or not his interpretations are correct concerning the function of B_2O_3, amply corroborates Orton's view.

Now does the fact that with the same RO and the same total SiO_2 content, glazes with 0.6 Al_2O_3 and 0.2 Al_2O_3 + 0.4 B_2O_3 are mattes at cone 7 and cone 07 respectively prove that B_2O_3 and Al_2O_3 function alike? The texture here is the sole coinciding result, and this not at the same cone. Is he justified from this coincidence in effect in this one series of trials in saying, "Based upon this fact, it seems practical to the author to place the B_2O_3 in matte glazes, not in the column with the silicic acid but in the column of the sesquioxides?" He had quoted Binns to this same effect from page 171, Vol. XI, of our Transactions. Both ignore all other proportions and oxides, the one author falling back onto an incorrect supposition that all cone 7 mattes must have an oxygen ratio of two, and the other to the so-called base, B_2O_3, rendering the glaze a "sesquisilicate."

The table of oxygen ratios just given, in which B_2O_3 is figured as a base, proves that the contention of neither of these gentlemen has a general application and that to argue from this one series as to the similarity in function of Al_2O_3 and B_2O_3 without taking the proportions and conditions into consideration is absurd.

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The report Stull has made concerning the total want of comparative effect of B_2O_3 and Al_2O_3 on cobalt pink amply offsets similar but contrary evidence presented by Dr. Singer.

For Dr. Singer's work on zeolites I have profound respect but am unable to discuss it for I know nothing of the chemistry involved. It may be that it is for this reason that I see in this portion of his work the only demonstration I know of in which a similarity in function of Al_2O_3 and B_2O_3 has been shown. I wish to draw attention to the fact, however, that these zeolites are very unstable and their constitution little understood, hence that they do not furnish positive proof concerning a similarity of rôle for B_2O_3 and Al_2O_3 in glazes. This Dr. Singer admitted.

The material evidence produced by Stull and Radcliffe,[8] and on which they make claim that in glazes of low oxygen ratio B_2O_3 functions as an acid, and in glazes of high oxygen ratio as a base, can not be questioned. It is in perfect keeping with similar evidence found by Fox and myself,[9] as may be seen in the descriptions of the trials[10] and also from the tables in summary (pp. 172–176). An error was made in our general conclusions in making too sweeping a statement[11] concerning the effect of B_2O_3 on crazing, and, for that matter, on devitrification. In this study by Fox and myself, B_2O_3 caused what we called devitrification in the first two groups, *i. e.*, those of lowest oxygen ratio, but counteracted it in the groups of higher oxygen ratios. Now the evidence is that in respect to both crazing and devitrification, B_2O_3 and Al_2O_3 have opposite effect in glazes of low oxygen ratio, and the same effect in glazes of higher oxygen ratios. Fox and I did not see this evidence when making our final summary and conclusions, and probably would not have seen it if Stull and Radcliffe had not developed and emphasized this same evidence concerning the effect of B_2O_3 on crazing in their research. So far as evidence is concerned, then, I have very good reasons for believing that their observations are correct,

[8] Trans. A. C. S., Vol. XII, p. 129.
[9] "Fritted Glazes," Trans. A. C. S., Vol. IX, p. 95.
[10] Loc. cit., pp. 124, 135, 140, 141.
[11] Ibid., p. 177.

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and the only reason I refer to the paper by Fox and myself is to make plain my reasons for faith that their evidence is correct.[12]

Is their *interpretation* of the evidence correct? Does it furnish proof that in glazes of low oxygen ratio B_2O_3 functions as an acid, and in glazes of high oxygen ratio it functions as a base? I hold that the evidence they present, although checked by similar evidence produced by myself, does not furnish proof concerning the chemical rôle of B_2O_3. In fact, this same doubt of proof in their evidence was evinced by Stull and Radcliffe themselves when they said:[13] "Although there are no absolute chemical proofs at hand, the following *theories*[14] are advanced from the foregoing evidence." Theories, hypotheses, deductions, conclusions and the like are not proofs; they are personal interpretations, assumptions or opinions. I say this, too, without the slightest disrespect to the evidence and conclusions (or theories) given by Stull and Radcliffe. In fact, their work deserves the same respect as any of that done on glazes by Seger and all other ceramists since Seger's day.

I clearly stated my estimate of the value of such empirical work when discussing Singer's paper.[15] I there said: "We have in this paper an excellent contrast between empiric and scientific work. The former is the kind we are used to reading in our Transactions. That sort of work has a decided value, but the evidence obtained is most largely circumstantial evidence, while the evidence obtained in scientific work, such as Dr. Singer has given us on zeolites, is positive evidence.

"The work done with glazes and colors does not warrant positive statements regarding the chemical nature or behavior of B_2O_3. In fact, all of this is admitted by Dr. Singer. His trials were glazes so compounded as to show the comparative influence of alumina and boracic acid. He also made color studies. The evidence he obtained is only indicative of *similarity*

[12] Minnemann also found increased crazing with increased content of B_2O_3 with low oxygen ratio, Trans. A. C. S., Vol. XIII, p. 523. See also discussion by Whitmer. Vol. XI, p. 277, and by Orton and others on p. 294 same volume.

[13] Ibid., p. 136.

[14] Not italics in the original.

[15] Trans. A. C. S., Vol. XII, p. 708.

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in action of Al_2O_3 and B_2O_3 but can give no positive conclusions as to the *chemical rôle* of B_2O_3 as compared with Al_2O_3."

All of this opinion, concerning the value of such data as proof, is in keeping with Dr. Singer's closing paragraph in which he says, "The question whether Al_2O_3 and B_2O_3 in glasses and glazes work in like manner as bases or as acids, I leave open," and with Stull and Radcliffe when they say that their evidence furnishes "no absolute chemical proofs."

I hold, therefore, that their evidence, from the nature of its kind, can not be taken as proof. It can be taken only as a basis for such theorizing and conjecturing concerning the chemical rôle of B_2O_3 as they give in their concluding paragraphs.

Are the "theories" advanced by Stull and Radcliffe backed by sound reasoning? I hold that they are not.

Staley,[16] as also Kerr,[17] has pointed out the illogic of such a "ring around the roses" argument that because the addition of an oxide to a glaze mixture causes crazing it must be an acid (or a base)[18] because addition of acids (or bases) causes crazing.

It is not intended, in this note, to enter into a discussion of the cause of crazing. This subject has repeatedly been theorized upon in our Transactions, and elsewhere, and, because the predominance of evidence is against the old "Coefficient" theory, we are now largely groping in the maze of several theories. The weight of the evidence, however, points clearly to the fact that the cause and cure of crazing can be credited to neither the basic nor to acid oxides as classes, nor can it be shown that the same oxide will alike effect crazing in all glaze mixtures.

Take, for illustration, the evidence given by Stull in his "Porcelain Glaze" study in this volume. He shows a curve which bounds the craze area, plotted on a chart in which increasing SiO_2 is the abscissa, and increasing Al_2O_3 is the ordinate. The craze boundary curve has a U shape. By starting from a point within the U, and proceeding either to the left (decreasing

[16] Trans. A. C. S., Vol. XIII, p. 124.

[17] Loc. cit., p. 138.

[18] Use of the alternative expression is because of the difference in assumption between Stull and the other writers as to whether it is the acids of the bases which produce crazing.

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SiO_2) or to the right (increasing SiO_2) we find that the glazes will pass from fit to craze. Or, starting from the same points within the U and proceeding upward (increasing Al_2O_3) we find continued fit, but on proceeding downward we soon find craze again. Are we to conclude from this that Al_2O_3 and SiO_2 both play the dual rôle of base and acid in glazes, the same as he argued for B_2O_3? Decidedly no!

This illustration emphasizes the want of logic (as pointed out by Staley, and by Kerr) in such a course of reasoning, and shows why we are finding more and more theories of crazing that do not involve the chemical nature or rôle of the varying oxides.[19]

Theories can not constitute proof, and inasmuch as Stull is basing his arguments for an acid rôle of B_2O_3 in glazes of low oxygen ratio, and for a basic role in glazes of high oxygen ratio, on other theories that in themselves involves unproved and much questioned hypotheses, his conclusions are worth no more than can be credited to personal opinions.

I will not enter into a further discussion of his adopted assumption that since in glazes of low oxygen ratio B_2O_3 causes crazing, it must be functioning as an acid, although his line of reasoning is directly opposite to the usual assumption concerning the effect of the acid constituents. I simply wish to draw attention to the fact that he had to reverse[20] the usual line of such reasoning in order to make his theories sound plausible.

No one has yet presented proof that B_2O_3 functions in glazes either as a base or as an acid. All who have attempted to obtain proof that B_2O_3 functions as a base admit their failure. I have no positive evidence on the case either way.

In conclusion, let me repeat that if one finds it convenient for any reason to write the B_2O_3 with the Al_2O_3 in the empirical molecular formula, there need be no further reason or argument for so doing. I maintain, however, that there is no inherent reason, other than convenience, that can be used in support of such a practice. The question of where to place B_2O_3 in the

[19] See Stull's "Crystallization Theory for Crazing," Trans. A. C. S., Vol. XII, p. 138.
[20] See Seger's "Collected Writings," p. 602, Amer. Cer. Soc. edition.

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formula is exactly like that concerning the coloring oxides. These, to simplify factory practice, I write as being added to the base glaze. The usual way has been to include the RO and R_2O coloring oxides in the RO group, and the R_2O_3 coloring oxides in the R_2O_3 group. This I found to be inconvenient, hence feel justified in not conforming to the old practice. For this same reason I prefer to write B_2O_3 as an acid and I feel I need no further justification for this.

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THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON.[1]

By R. E. BROWN, Mt. Savage, Md.

INTRODUCTION.

Classification of Opacifiers.—Opacifiers for the purposes of this work are divided into two classes: (1) partial opacifiers, and (2) absolute opacifiers.

In the first class are included bone ash, fluorite, cryolite, and silica. Bone ash is rarely employed in enamels, but the remaining three, especially the silica, are invariably used. Fluorite and cryolite are advantageous, commercially, both from the standpoint of their low fusibility and their fluorine content. The latter gives them the property of acting as weak opacifiers, thereby decreasing the amount of absolute opacifier needed.[2] The silica, as is shown by the following work, has no opacifying tendencies in itself in this type of glasses but emphasizes and increases the opacity brought about by certain opacifiers proper.

In the second class, the opacifiers, *per se*, are arsenious oxide, zirconium oxide, tin oxide and antimony oxide. Arsenious oxide finds a very limited use, being employed only for decorative work on jewelry and art ware. Zirconium oxide is not widely used; while some consider it too expensive for commercial work, others regard it a cheap opacifier as a substitute for tin oxide.[3] Tin oxide is by far the most widely used of the opacifiers, and is employed not only in the enameling of sheet iron and cast iron, but in the enameling of clay products as well.

Antimony oxide has had, to date, only an extremely limited use as an opacifier. It has been used to some extent in Germany in conjunction with zinc oxide as a substitute for tin oxide.[4] It has been used in this country to some extent, and in one case its use in conjunction with other ingredients is patented as "a substitute for tin oxide."[5] In a "Note on White Antimony

[1] Abstract of a thesis fulfilling part of the requirements for the degree of Bachelor of Science in Ceramics, University of Illinois.

[2] Mayer and Havas, Sprechsaal, XLII, 460–461.

[3] La Ceramique, 11, 100–101. Keram Rundschau, XVI, 89–91, 135–139.

[4] Ph. Eyer, Stahl und Eisen, XVIII, 1097, 1099.

[5] U. S. Patent, 932,839.

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Enamels," Bock points out the dangers of the use of antimony oxide in enamels for cooking vessels, but no mention is made of its employment in enamels for cast iron.[6]

The most expensive constituent of the ordinary commercial enamel is the opacifying agent, tin oxide, both by reason of the high market price and the quantity employed. The prices of antimony oxide and tin oxide in barrel lots are at present $10^1/_2$ and 45 cents per pound, respectively.

Object of Work.—It was with a view to using the cheaper opacifier for cast iron enamels that this work was undertaken. The work attempts to determine, in a practical way, the conditions under which antimony oxide may be used in enamels.

EXECUTION OF WORK.

Preparation of the Enamels.—In carrying out a series the ingredients of the two extremes of a series were weighed up and mixed thoroughly by passing 5 or 6 times through a 20 mesh screen. The batch was next put into a small fire clay crucible (capacity about 250 grams of the raw batch) and fritted in a pot furnace, fired by a blast lamp using artificial gas and compressed air as fuel. After melting and becoming relatively free from bubbles the contents were poured into water. It was then dried, again put into the crucibles and refritted, care being taken in this second fritting to prolong the heating to such length of time that no bubbles were given off. As soon as bubbles had ceased to form, the contents were again quenched by pouring into water. The shattered glass was dried and then ground in 8 inch, porcelain, ball mills so as to pass a 200 mesh sieve.

The two extremes of a series, now in a powdered form, were weighed out in the proper proportions to form the intermediate enamels. These were now mixed by rubbing 5 or 6 times through a 60 mesh sieve.

The Ingredients.—The raw ingredients employed in introducing the following constituents with the molecular weights used were as follows:

ZnO: Introduced as zinc oxide (81).

PbO: Brought in as red lead Pb_3O_4 (685).

[6] Chem. Ztg., XXXII, 516–517.

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BaO: Where employed, was brought in by barium carbonate (197).

CaO: Brought in by fluorite (78), whiting (100), and hydrated lime (74).

Na_2O: Introduced as sodium carbonate (106), borax (382), and cryolite (210).

K_2O: Brought in by potassium nitrate (101) and potash feldspar (557).

MgO: Brought in by magnesium carbonate (84) and magnesium oxide (40).

Al_2O_3: Potash spar (557) was used as the main source of alumina. Small amounts of cryolite, Na_3AlF_6 (210) were also used.

B_2O_3: This was brought in by using borax (382) in the cover enamels and as borax and boric acid (62) in the ground coats.

SnO_2: Brought in as tin oxide (150).

Sb_2O_3: Introduced as white oxide of antimony (288).

SiO_2: Brought in as potash feldspar (557), and as flint (60).

In addition to the above ingredients, ammonium carbonate was used in some of the enamels of the later series. This volatilizes readily and serves as a clarifier of bubbles in the glass during fritting.

Trial Pieces.—The trial pieces were small circular discs $^1/_8''$ thick and 2″ in diameter with a raised center. The iron used for casting these trials did not prove to be of a very satisfactory grade as it frequently produced large bubbles or blisters in the enamels, probably due to the sulphur content of the iron.

The trials were cleaned by pickling for 20–30 minutes in a dilute solution of hydrochloric acid so as to remove the scale and any oxide present. After this they were washed and scrubbed and then dipped in a dilute solution of sodium carbonate so as to neutralize all of the acid. They were then scrubbed and washed again, the surface water was wiped off, and the trials were put into a warm oven. Even with this seemingly thorough treatment, the coat of carbon (left by dissolving the iron) was not entirely removed, and hence gave rise to bubbles during the burning process. Another method of cleaning the iron, used in the latter part of the work, proved very effective. In this, the iron

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was pickled as before and then put into a ball mill with sand and water; thus all of the carbon was effectually removed with the result that less trouble as regards bubbling was experienced.

The ground coat was applied to the trials by dipping, care being taken to secure a thin coat that was as uniform as possible.

Composition of the Ground Coat.—The ground coat chosen was of the composition shown:

$$\left.\begin{array}{l} 0.30\ K_2O \\ 0.24\ Na_2O \\ 0.159\ CaO \\ 0.219\ MgO \\ 0.081\ PbO \end{array}\right\} \left.\begin{array}{l} 0.297\ Al_2O_3 \\ 0.31\ B_2O_3 \end{array}\right\} 2.19\ SiO_2$$

Batch weights: 15 flint; 30 potash feldspar; 10 boric acid; 5 KNO_3; 5 Pb_3O_4; 2.2 $Ca(OH)_2$; 2.3 MgO; 10.0 cryolite; 1.0 fluorite.

The trial piece, after being slush coated and dried, was placed in the furnace, which had been heated to the temperature of burning. As soon as the iron had attained a sufficient heat for fusing the ground enamel, it appears to "melt" not unlike a coat of frost or snow. This commences at one spot and soon has extended over the whole trial. The trial now has a glossy appearance. Almost coincident with this, innumerable bubbles are formed which "break" at once. This continues for a short time, after which the glossy coating or glass smooths down. It is at this point, in the writer's judgment, that the burning of the ground coat is complete. If the trial is not removed at once, larger bubbles are formed, but the glass is then decidedly more viscous than when the preliminary bubbles were formed. When they break, if they break at all, they leave a rough slag on the surface of the trial as is shown by cooling the trial piece.

Burning the Enamels.—The furnace used for the enameling was of the open-fired type, *i. e.*, without a muffle chamber, and was fired by the use of artificial gas and compressed air as fuel. Although this is not the type of furnace best suited for this kind of work, it was the only one available and there was no time for the construction of a more suitable one. The temperature of burning was measured by a Le Chatelier pyrometer, the couple of which was inserted so that its junction point was at the side

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of the trial. The holder for the trial piece consisted of a bar of iron "upset" at one end and so shaped as to fit on the inside of the trial piece.

Series I.

REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN A TIN ENAMEL.

This series was carried out by replacing the tin oxide in an enamel similar to that given by Riddle in his "Types of Enamels for Enameling Cast Iron Sanitary Ware," Trans. A. C. S., Vol. IX, with antimony oxide, thus:

$$\left.\begin{array}{l} 0.25\ Na_2O \\ 0.10\ MgO \\ 0.15\ PbO \\ 0.15\ BaO \\ 0.15\ K_2O \\ 0.05\ ZnO \\ 0.15\ CaO \end{array}\right\} \left\{\begin{array}{l} 0.15\ Al_2O_3 \\ 0.20\ B_2O_3 \end{array}\right\} 1.00\ SiO_2 \quad 0.15\ SnO_2\text{–}0.075\ Sb_2O_3$$

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	$BaCO_3$	CaF_2	ZnO	$MgCO_3$	Borax	K. Spar	Flint	SnO_2	Sb_2O_3
1	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.15	0.00
2	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.1125	0.0188
3	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.075	0.0375
4	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.0375	0.056
5	0.15	0.05	0.15	0.15	0.05	0.10	0.10	0.15	0.10	0.00	0.075

Description of Trials.—No. 1 is a good enamel and is a typical tin enamel. All of the rest of the series, with the possible exception of No. 2, are very poor. A peculiar "puckery" or matte texture exists, the surface is rough and uneven, and the enamel flies off in patches, resembling shivering of clay ware. In the trials of enamels 3 and 4, the "puckery" effect is partially overcome by raising the burning temperature. The shivering is also lessened by this treatment. It is also evident in this series as well as in the rest of the work that where an enamel is applied, too thick shivering is more likely to occur.

Thinking perhaps that the "puckery" effect might be overcome partially by making a more easily fusible enamel it was

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decided to run a series with a more fusible RO combination. It was also suggested that the "puckery" effect might be due to the barium which reacted with the sulphur present in the Sb_2O_3.[7] Some of the Sb_2O_3 was tested and found to contain sulphur.

A series embodying the two above ideas was accordingly carried out as given below. Although it was not conducted strictly on a scientific basis it is sufficient to show in a practical way the desired effect.

Series II.

VARIATION OF BARIUM OXIDE AND ITS EFFECT ON ANTIMONY OXIDE.

0.25–0.54 Na_2O
0.10–0.00 MgO
0.15–0.15 PbO
0.15–0.16 K_2O
0.05–0.05 ZnO
0.15–0.10 CaO
0.15–0.00 BaO

0.15–0.16 Al_2O_3
0.20 B_2O_3

1.00 SiO_2
0.075 Sb_2O_3

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	$BaCO_3$	CaF_2	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	$MgCO_3$	Spar	Flint	Sb_2O_3
1.....	0.15	0.05	0.15	0.15	0.05	0.00	0.00	0.00	0.10	0.10	0.15	0.10	0.075
2.....	0.21	0.05	0.10	0.10	0.05	0.02	0.02	0.03	0.10	0.07	0.148	0.14	0.075
3.....	0.29	0.05	0.05	0.05	0.05	0.04	0.04	0.07	0.10	0.03	0.136	0.18	0.075
4.....	0.35	0.05	0.00	0.00	0.05	0.06	0.06	0.10	0.10	0.00	0.13	0.22	0.075

Description of Trials.—The "puckery" effect has decreased toward the end of the series which contains no barium and in No. 4 is not present at all. This enamel is a fair enamel which adheres well. No. 1 is somewhat shivered. This series shows from a practical standpoint that barium should not be used to any very large extent in an enamel where there is a contact with sulphur gases. Its use, however, in enamels where tin is used as an opacifier is very much desired, owing to its ability to decrease shivering.

[7] Sb_2O_3 is prepared from stibnite, Sb_2S_3, by roasting in air, hence sulphates are formed which, if not entirely removed, would combine with the barium compounds.

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Series III.

VARIATION OF THE SILICA CONTENT.

This series was varied between the limits of 1.00 and 2.00 equivalents of silica as shown:

$$\left.\begin{matrix} 0.10\ CaO \\ 0.54\ Na_2O \\ 0.15\ PbO \\ 0.16\ K_2O \\ 0.05\ ZnO \end{matrix}\right\} \quad \left\{\begin{matrix} 0.16\ Al_2O_3 \\ 0.20\ B_2O_3 \end{matrix}\right\} \quad \left.\begin{matrix} 1.00\text{–}2.00\ SiO_2 \\ 0.075\ Sb_2O_5 \end{matrix}\right\}$$

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_5
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.22	0.075
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.345	0.075
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.47	0.075
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.595	0.075
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.72	0.075
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.845	0.075
7.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	0.97	0.075
8.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.095	0.075
9.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.075

Description of Trials.—Nos. 1, 2 and 3 have an egg shell-like texture but otherwise are fair enamels. The trials of enamels Nos. 4 and 5 are better and do not show the above texture to such a degree. No. 6 is a fair enamel but is a trifle dull. No. 7 is a good enamel and adheres well. It is whiter and has a better gloss than the average commercial enamel. Enamel No. 8 is whiter than No. 7 and has a better gloss. A few of the trials shiver somewhat, showing that the silica is a trifle too high. Enamel No. 9 has shivered still more, but on the trials where it held, it is the whitest and most brilliant of the series. Enamels Nos. 8 and 9 have an exceptionally white color and are more than the equal of the average tin enamel in this respect.

The result of this series seems to show that the last two enamels are too high in silica and also that a silica content of over 1.85 equivalents is conducive in shivering. The burning temperature rises as the silica content increases; but this heat,

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even with the enamels containing 2.0 SiO_2, did not cause the iron to deteriorate to any visible extent. As silica increases, the whiteness is increased, and it is evident that a sacrifice must be made of part of the whiteness in order to obtain enamels that do not shiver.

Series IV.

VARIATION OF ALUMINA.

This series was run between the limits of 0.1 and 0.2 equivalent of Al_2O_3. To bring in the Al_2O_3 in combined form, *i. e.*, as spar, it was necessary to change the RO with respect to K_2O and Na_2O thus:

0.16–0.20 K_2O 0.15 PbO 0.10 CaO 0.54–0.50 Na_2O 0.05 ZnO	0.10–0.20 Al_2O_3 0.20 B_2O_3	1.80 SiO_2 0.075 Sb_2O_5

Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	K_2CO_3	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_5
1....	0.35	0.05	0.05	0.06	0.06	0.06	0.10	0.10	0.07	1.38	0.075
2....	0.342	0.05	0.05	0.049	0.06	0.06	0.10	0.10	0.09	1.26	0.075
3....	0.334	0.05	0.05	0.038	0.06	0.06	0.10	0.10	0.11	1.14	0.075
4....	0.326	0.05	0.05	0.025	0.06	0.06	0.10	0.10	0.13	1.02	0.075
5....	0.318	0.05	0.05	0.013	0.06	0.06	0.10	0.10	0.15	0.90	0.075
6....	0.31	0.05	0.05	0.00	0.06	0.06	0.10	0.10	0.17	0.78	0.075

Description of Trials.—All enamels of the series are good enamels with whiteness increasing toward No. 6, *i. e.*, with increase of Al_2O_3. The temperature required for maturing increases, however, with the Al_2O_3. The best enamel of the series, taking burning temperature, whiteness, gloss, and adhesive properties into consideration, is No. 4 containing 0.16 Al_2O_3.

Series V.

VARIATION OF ANTIMONY OXIDE.

This series as well as the remaining two series was carried out in two parts, A and B, the two parts being practically alike.

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except for the silica content. Part B was carried out first and the limits of Sb_2O_3 were not high enough, hence these were changed in A.

Series V, A.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\left\{\begin{matrix}0.16\ Al_2O_3\\0.20\ B_2O_3\end{matrix}\right\}\left\{\begin{matrix}1.8\ SiO_2\\0\text{–}0.14\ Sb_2O_3\end{matrix}\right.$$

Series V, B.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\left\{\begin{matrix}0.16\ Al_2O_3\\0.20\ B_2O_3\end{matrix}\right\}\left\{\begin{matrix}2.0\ SiO_2\\0\text{–}0.11\ Sb_2O_3\end{matrix}\right.$$

V, A. Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.00
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.02
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.04
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.06
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.08
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.10
7.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.12
8.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.02	0.14

V, B. Batch formulae (in equivalents).

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.00
2.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.022
3.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.044
4.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.066
5.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.088
6.....	0.35	0.05	0.05	0.06	0.06	0.10	0.10	0.13	1.22	0.11

Description of Trials.—The trials of enamel 1 A have but

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slight opacity. No. 2 A has a trifle more and so on up the series, Enamel No. 3 A has a fair opacity, No. 4 A and 5 A are good enamels, No. 5 A being the whitest. No. 6 A is a good enamel. It is whiter than No. 5 but is not quite so glossy. No. 7 is a good enamel and is a trifle "matte" in texture. No. 8 has a beautiful matte texture and differs from all the rest of the series in this respect. One of the trials, however, shows a tendency to shiver but this may possibly be due to the mode of application. Enamel No. 5 is the best of the A part of the series, taking gloss, finish, and general appearance into consideration, while for a dull or matte texture No. 8 is the best. Enamels No. 7 and 8 require a higher temperature for burning, thus indicating that high antimony decreases the fusibility.

With part B of the series shivering is more evident in every case. The enamels which held are, however, of greater brilliancy and opacity, enamel No. 2 of A being identical in appearance with No. 1 of B. Enamels 2, 3 and 4 of part B are practically the same as 3, 4 and 5 of part A respectively. From this we would conclude that 0.016 equivalent of Sb_2O_3, in this range of silica content, has about the same opacifying effect as 0.02 equivalent of silica.

Series VI.

REPLACEMENT OF ANTIMONY OXIDE BY TIN OXIDE IN AN ANTIMONY ENAMEL.

This series, also using two different equivalents of silica, was carried out as follows:

VI, A.

0.16 K_2O		
0.05 ZnO	0.16 Al_2O_3	1.80 SiO_2
0.10 CaO		
0.15 PbO	0.20 B_2O_3	0.075 Sb_2O_3–0.15 SnO_2
0.54 Na_2O		

VI, B.

0.16 K_2O		
0.05 ZnO	0.16 Al_2O_3	2.0 SiO_2
0.10 CaO		
0.15 PbO	0.20 B_2O_3	0.075 Sb_2O_3–0.15 SnO_2
0.54 Na_2O		

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Batch formulae (in equivalents).

VI, A.

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3	SnO_2
1....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075	0.00
2....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.056	0.038
3....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.038	0.075
4....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.019	0.1125
5....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.00	0.15

VI, B.

1....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075	0.00
2....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.056	0.038
3....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.038	0.075
4....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.019	0.1125
5....	0.35	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.00	0.15

Description of Trials.—All enamels of the A part of the series adhere tenaciously and are good enamels. Enamel No. 1 has more opacity and whiteness than No. 5, these two properties decreasing uniformly between these extremes. The antimony enamel requires a slightly higher temperature for maturing, but not to such extent as to be detrimental to the iron.

In the B part of the series shivering is much in evidence, due to the increased silica. Enamels Nos. 1 and 2 have good opacity but Nos. 3 and 4 are much inferior in this respect. In enamel No. 5 the silica has dissolved the SnO_2 almost entirely. Taking the results of this series we would conclude that SiO_2 at the higher limit is opposite in effect with regard to Sb_2O_3 and SnO_2. In the case of Sb_2O_3 the opacity, whiteness and brilliancy are increased, while with SnO_2 these properties, notably the opacity, are decreased. Shivering, however, is increased in either case. The results obtained in part A of the series are not in accord with those of Riddle whose high limit of silica was 1.25 equivalents. In enamel No. 5 part A as given above, a good white enamel was obtained using 1.8 equivalents of silica.

It might be interesting to note also at this point, the behavior of the enamels on wrought iron. The enamels of part A were applied to iron washers, and although they had not been

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previously cleaned, the enamels held perfectly and were of good whiteness, brilliancy and texture.

Series VII.

VARIATION OF BORIC OXIDE.

This series employs two equivalents of silica and the Na_2CO_3 content is varied in order to reach the lower limit of B_2O_3 still maintaining the same ratio.

VII, A.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\left.\begin{matrix}0.16\ Al_2O_3\\0.10\text{–}0.40\ B_2O_3\end{matrix}\right\}\begin{matrix}1.80\ SiO_2\\0.075\ Sb_2O_3\end{matrix}$$

VII, B.

$$\left.\begin{matrix}0.16\ K_2O\\0.05\ ZnO\\0.10\ CaO\\0.15\ PbO\\0.54\ Na_2O\end{matrix}\right\}\left.\begin{matrix}0.16\ Al_2O_3\\0.10\text{–}0.40\ B_2O_3\end{matrix}\right\}\begin{matrix}2.00\ SiO_2\\0.075\ Sb_2O_3\end{matrix}$$

VII, A.

Batch formulae (in equivalents)

No.	Na_2CO_3	R. Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K. Spar	Flint	Sb_2O_3
1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.02	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.02	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.02	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.02	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.02	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.02	0.075
7.....	0.25	0.05	0.05	0.03	0.06	0.10	0.2	0.13	1.02	0.075

VII, B.

1.....	0.4	0.05	0.05	0.03	0.06	0.10	0.05	0.13	1.22	0.075
2.....	0.375	0.05	0.05	0.03	0.06	0.10	0.075	0.13	1.22	0.075
3.....	0.350	0.05	0.05	0.03	0.06	0.10	0.10	0.13	1.22	0.075
4.....	0.325	0.05	0.05	0.03	0.06	0.10	0.125	0.13	1.22	0.075
5.....	0.300	0.05	0.05	0.03	0.06	0.10	0.150	0.13	1.22	0.075
6.....	0.275	0.05	0.05	0.03	0.06	0.10	0.175	0.13	1.22	0.075
7.....	0.250	0.05	0.05	0.03	0.06	0.10	0.200	0.13	1.22	0.075

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Description of Trials.—All enamels of part A adhere well and are good white enamels up to No. 6. Nos. 6 and 7 have a yellowish cast and are not all desirable enamels. Bubbling is also evident in the enamels of higher B_2O_3 content. Enamel No. 1 is the whitest of the five enamels.

The results obtained in part B are substantially the same as those of part A. The enamels are whiter, however, than the ones of the same B_2O_3 content and the yellowish cast of enamels 6 and 7 of part A has disappeared in the corresponding enamels of part B. Shivering is present to quite a large extent in part B, due to the high silica. As in part A, bubbling is prominent in the enamels of the higher B_2O_3 content. The difference in whiteness of the high and low B_2O_3 enamels in part A is not so pronounced in this part of the series. Enamels B 1 and B 7 have very little difference in whiteness, B 1 being a little the whitest. The difference in maturing temperature is however quite large and the tendency to bubbling is more evident.

The results indicate that the lower the B_2O_3 the better and whiter are the enamels. The limits for desirable enamels are about 0.15–0.30 B_2O_3.

LIMITS OF THE INGREDIENTS.

The limits of the ingredients and their effects established by this work are as follows:

SiO_2: The effect of silica is to increase brilliancy, whiteness, acid-resisting properties and gloss. If increased too high, shivering takes place and the maturing temperature is too high. The limits are about 1.65–1.85 equivalents, those nearer the higher limit being the preferable.

Al_2O_3: Increased Al_2O_3 increases the temperature for maturing and gives whiter enamels. The high limit is around 0.18 equivalent. The low limit was not established but for commercial enamels is probably about 0.13 equivalent.

Sb_2O_3: The effect of Sb_2O_3 is to increase the maturing temperature, and to increase the whiteness and opacity when employed between the limits of 0.0–0.09 equivalent Sb_2O_3. If used between the limits of 0.1–0.14 equivalent the enamels are dull at the lower limits and matteness increases at the higher.

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At the high limit, 0.14 equivalent, shivering is likely to occur.

For brilliant enamels of good opacity and texture the limits are 0.06–0.09 equivalent, about 0.075 being preferable.

SnO_2: No variation of the SnO_2 content was made but a good enamel was obtained using 0.15 equivalent of SnO_2.

B_2O_3: The effect of increased B_2O_3 is to lower the maturing temperature, to increase the tendency to produce bubbles, to decrease the whiteness when used above a certain limit, increase gloss, and to increase the solubility of the enamel. The limits are about 0.15–0.3 equivalent, those nearer the lower limit being preferable.

BaO: The effect of BaO in Sb_2O_3 enamels is to produce a "puckery" or matte effect. This is no doubt due to the sulphur arising from the Sb_2O_3 and the fuel gases, which comes in contact with the barium compounds.

The most likely enamel taking all points into consideration is:

$$\left.\begin{matrix} 0.16\ K_2O \\ 0.05\ ZnO \\ 0.10\ CaO \\ 0.15\ PbO \\ 0.54\ Na_2O \end{matrix}\right\} \left.\begin{matrix} 0.16\ Al_2O_3 \\ 0.20\ B_2O_3 \end{matrix}\right\} \begin{matrix} 1.80\ SiO_2 \\ 0.075\ Sb_2O_3 \end{matrix}$$

DISCUSSION.

Professor Staley: Why do you not include the fluorine in your formula? No one will be able to calculate the batch from the formula unless you do so. Moreover, it makes a vast difference whether an enamel contains a small or a large amount of this element.

Mr. Brown: I do not think it is necessary. I introduced it as cryolite, using 0.06 equivalent of cryolite throughout.

Professor Staley: Mr. Brown, I just want to ask one more question. Did you get an absolutely pure white enamel, or was it of a greenish or bluish tint? There have been many attempts made to use antimony in place of tin oxide in cast iron enamels, but it has never given a satisfactory white. They get a tint they call white, but it is not a commercial white. Do you have any idea of how to avoid getting that greenish, bluish white so characteristic of antimony oxide?

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Mr. Brown: I did not carry on work to eliminate the cast you speak of. The cast was not present to an aggravated extent that I could see. A number of others said the same thing. There is a slight bluish cast or tint in some of the trials.

Professor Staley: In your final enamel as well as in all the others?

Mr. Brown: It was not so pronounced in this case, but more so in the enamels of higher silica content.

Mr. Burt: I noticed in speaking of the enameled iron industry they always speak of dusting the enamel on and I would like to get a little description of what the mechanical process is—of what is involved in this dusting on of the glaze.

Professor Staley: In a paper ("The Manufacture of Enameled Iron Sanitary Ware," Trans. A. C. S., Vol. VIII, p. 172) I published several years ago, you can find a description of the ordinary method of making a piece of enameled cast iron. The only difference between the method described there and the method used at present is the use of a mechanical agitator.

Mr. Burt: What mesh sieve do you use?

Professor Staley: The sieve is a fifty- or sixty-mesh sieve.

Mr. Brown: I would like to ask Professor Staley what his opinion is of the fluorine in a fused enamel—whether it is volatilized or whether it is retained in the enamel. I have read of several instances where they analyzed for fluorine and found it in the enamels in small quantities.

Professor Staley: That is all a matter, in my mind, of how hard, how long, and how hot you heat the enamel. You can volatilize it all, or you can have the larger portion of it stay in. If it is all volatilized you have no opacifying effect from the use of fluorides. In cast iron enamels that are heated or fritted in the ordinary length of time, the large bulk of fluorine stays in.

NOTE PREPARED AFTER READING THE PAPER.

Professor Bleininger: It seems to me that Mr. Brown has solved his problem satisfactorily. He has accomplished two things, *viz.*, the production of a white enamel which compares favorably with the best tin enamels, in the opinion of impartial observers, and he likewise has shown clearly the kind of enamel

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required for the use of antimony as an opacifier, which differs somewhat from the common type.

As regards the poisonous quality of antimony compounds, Rickmann, Sprechsaal, XLV, 115–117, says that during an experience of ten years the use of metasodium antimonate has not proven injurious. However, he points out that the antimony oxide compounds (tartar emetic, etc.) are poisonous. For cast iron enamels, therefore, the use of $Na_2Sb_2O_3$ might be a perfectly feasible solution.

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THE NECESSITY OF COBALT OXIDE IN GROUND-COAT ENAMELS FOR SHEET STEEL.

By ROBERT D. LANDRUM.

There has been a great deal of discussion recently in German ceramic literature over the function of the ground coat and especially as to the necessity of cobalt being present in such an enamel. As the durability of an enameled ware is primarily dependent upon the physical properties of this fundamental coating, it might be well to review what has been said upon the subject.

In the Transactions of the American Ceramic Society, XI. p. 115, J. B. Shaw says that cobalt-containing grounds have the advantage that they change color during burning, the iron taken up from the steel destroying the blue cobalt color. "The ground coat is considered well burnt when the blue color is no longer visible. It seems to be quite generally believed that CoO has a great affinity for iron and that a good ground coat cannot be made without using CoO." Shaw goes on to say that from his experiments along this line he feels perfectly safe in stating that this belief is ungrounded.

About the only other time that this subject is mentioned in the Transactions is by J. H. Coe, Volume XIII, p. 549, and he states that the value of cobalt oxide in the ground coat for cast iron is doubtful.

Dr. Grunwald in his book "Enameling on Iron and Steel," p. 22, says: "Cobalt oxide possesses valuable physical characteristics which make it suitable for the preparation of ground (coat) enamels, for these derive the property that their coefficients of expansion are as near as possible the same as sheet iron." This is disputed by M. Mayer and B. Havas[1] who find that ground coat enamels have a much lower coefficient of expansion than that of sheet steel.

Dr. Vondracek, in the Sprechsaal, 1909, No. 14, seems to have first propounded the theory of the function of cobalt in a ground-coat enamel which is most popular at present. He considers

[1] Chem. Ztg., Vol. XXXIII, p. 1314.

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that the iron, at the melting temperature of the ground coat, is oxidized at the expense of the cobalt oxide and that the latter, or rather the cobalt silicate, is changed to a compound of lower oxygen content, or is even reduced to the metal. As a result of this, the clean surface of the iron is attacked so that the enamel joins very intimately with the metal and the danger of the chipping off of the enamel coats is lessened. In another place, Dr. Vondracek, although he repeats that cobalt improves the adhesiveness of enamels, says: "I have, notwithstanding, often obtained a very adhesive ground-coat enamel without using cobalt oxide."[2]

Philip Eyer in his book "Die Eisenemailierung," pp. 10–12, says: "The idea of adding cobalt oxide to the glaze so that it will go into combination with the iron is faulty, for a good, adherent ground-glaze can be prepared without the use of that oxide. However, the application of such a ground coat is impossible in practice." Also in writing of cast-iron enamels in the "Glashutte," Vol. XLI, pp. 737–8, 764–5, he says that cobalt and nickel are necessary as they form a weak alloy with the iron.

C. Tostman, in the Keramische Rundschau, XIX, pp. 5, 65 and 107, discusses this subject and emphasizes especially, what is, in the writer's opinion, the best argument as to the necessity of cobalt in a ground coat. He agrees with Shaw that cobalt acts as an indicator for correctly burning the enamel. He says in part:

"Only in cobalt oxide grounds does a blue color appear on smelting. If one should discontinue the heating just at this point, it would not adhere firmly enough to the steel, even though it had already become molten and glass-like. One can also burn it so long that the color becomes black. Now how is this (definite) color change, which is so markedly essential for a proper adhesion to be explained? The only explanation I find for it is that the enamel has taken up the iron from the surface (of the black shape) in some form of oxidation."

He goes on to state that while this oxygen might come from the air in the muffle, it is more probable that it is given up by the oxide of cobalt, which is in turn reduced to metal. "These

[2] See Chem. Ztg., XXX, 575–7.

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small amounts of very finely divided metallic cobalt could then perhaps form a very porous alloy with the iron on the surface of the shape. To this, the enamel would be able to adhere firmly, while the silicate flux would take the place of the cobalt which alloyed with the iron." He gives as an argument that this oxygen is furnished to the iron by the cobalt and not from any other source, the fact that in ground coats, which are not colored by cobalt, "an exceedingly smaller change of color takes place during the burning." He also mentions the fact that the addition of borax to an enamel causes it to chip and the further addition of cobalt oxide seems to correct this.

Dr. Bela Havas[3] replies to Tostman that he agrees with him that the cobalt silicate in the ground coat is reduced to a lower stage of oxidation and, as previously published by him in coöperation with M. Mayer,[4] this is indicated by the change of color of the enamel coating from blue to green. However, he states that it is improbable that the reduction of the cobalt silicate at the temperatures involved would go far enough to produce metallic cobalt.

The writer has no new theories to offer, but he is very strongly of the opinion that cobalt is a necessary ingredient in a successful ground coat for two reasons, which have been given above:

First, it is an excellent indicator which will inform the "burner" exactly the point at which his charge of ware is correctly burned.

Second, whatever may be the reason, the fact remains that cobalt grounds adhere more firmly to the steel than those not containing this metal, and it is the opinion of the writer that any non-cobalt ground coat can be improved in its adhesive properties by the correct addition of cobalt to its formula.

To illustrate this a ground coat was prepared which is practically a transparent glaze. When it is coated on a piece of ware the bright steel surface shows through the glaze and makes this appear a very light colored coating (see Fig. I, 1). The

[3] Sprechsaal, XLIV, 72–3.
[4] Ibid., XLIII, 727–9.

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composition is practically the same as that of the Mayer and Havas ground No. 1 as given in the Sprechsaal, 1909, No. 34.

M-H. GROUND COAT NUMBER ONE.[5]

Batch mix		Graphic formula		
Feldspar	36.34%	0.642 Na_2O		2.256 SiO_2
Borax	35.64%	0.080 K_2O		
Quartz	14.38%	0.243 CaO	0.204 Al_2O_3	0.629 B_2O_3
Soda	7.42%	0.025 MnO		
Fluorspar	5.34%	0.010 CoO		0.231 F_2
Manganese oxide	0.65%			
Cobalt oxide	0.23%	ORb 4.0, ORb 7.0, SiO_2/B_2O_3 3.6		

Milled with 6 per cent. clay and $2^1/_2$ per cent. dissolved borax.

A cobalt ground coat has been prepared which has the same chemical composition except that 0.03 equivalent part of CaO has been replaced 0.03 equivalent part of CoO (see Fig. I, 2). This enamel has been made as follows:

COBALT GROUND COAT.[5]

Batch mix		Graphic formula		
Feldspar	36.42%	0.642 Na_2O		2.260 SiO_2
Borax	35.54%	0.080 K_2O		
Quartz	14.38%	0.213 CaO	0.203 Al_2O_3	0.628 B_2O_3
Soda	7.42%	0.040 CoO		
Fluorspar	4.64%	0.025 MnO		0.201 F_2
Manganese oxide	0.65%			
Cobalt oxide	0.95%	ORb 4.0, ORa 7.0, SiO_2/B_2O_3 3.6		

Milled with 6 per cent. clay and $2^1/_2$ per cent. dissolved borax.

Each of these enamels has been coated with two white cover coats and then tested under the hammer (see article on white enamels), and it is to be noticed that the non-cobalt ground coat leaves the steel entirely bright and bare (see Fig. I, 3), while the one containing cobalt still adheres in concentric ridges (see Fig. I, 4). It is very evident that the cobalt must cause this extra adhesiveness.

[5] The same materials and method of manufacturing and a similar arrangement of data have been used as in "Comparison of Ten White Enamels for Sheet Steel," this volume.

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Fig. I.

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DISCUSSION.

Mr. Landrum: As an example of the reduction of a metal oxide (or silicate) in an enamel coating by the steel of the shape it may be interesting to examine a sample dish coated with the following enamel:

$$\left.\begin{array}{l} 0.451\ Na_2O \\ 0.019\ K_2O \\ 0.123\ CaO \\ 0.285\ ZnO \\ 0.122\ CuO \end{array}\right\} \quad 0.111\ Al_2O_3 \quad \left\{\begin{array}{l} 0.886\ SiO_2 \\ \\ 0.282\ B_2O_3 \\ \\ 0.123\ F_2 \end{array}\right.$$

Milled with $6^1/_2$ per cent. clay.

This enamel when used as a cover coat (separated from the steel by a ground-coat enamel) is *green* but when applied directly to the steel becomes *red* through the reduction of the copper compound. It may be observed on the sample which has been dented in the testing machine that some of the copper compound has been reduced to the metal and that this is plated on the steel surface.

Mr. Purdy: You have tried oxides other than cobalt? Have you tried nickel, for instance?

Mr. Landrum: I have tried oxide of nickel and it works fairly well, but does not promote adhesiveness to as great a degree as does the oxide of cobalt. It is best used in combination with that oxide.

Mr. Purdy: There is no actual oxygen for it to give up.

Mr. Landrum: We have nickelic and nickelous compounds, and the change may be from one to the other and not necessarily a change of the oxides; then, too, the conclusion might be drawn that the reduction is to metallic nickel. In the case of the enamels under discussion, it is easy to see that the one containing cobalt (see vessel 4 in illustration) *does* adhere to the steel after being dented while the one which does not contain cobalt (vessel 3) *does not* adhere but leaves the steel surface bright.

Prof. Staley: You will have to look at it with a microscope.

Mr. Landrum: I have examined this and other cobalt grounds under the microscope and have not been able to see any evidence of an alloy being present. The dark particles remain-

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ing after the dish is dented have a gloss that would lead one to think that they are particles of the glaze rather than of metal. Microscopic examination is difficult as it is practically impossible to get a good cross section of an enameled steel sheet.

Prof. Staley: In other words, this alloy theory is used just because it fits in—because it is within reason?

Mr. Landrum: Yes, and even then there is a doubt that it is within reason at enameling temperatures.

Mr. Purdy: In our transactions I stated as my opinion that cobalt in the ground coat merely furnished a mechanical means of holding the enamel onto the iron. It is easy to enamel most metals directly, but very difficult to enamel iron. The cobalt is merely suspended in the ground coat furnishing the required easily enameled "go between."

Mr. Landrum: This may be true and would be a good explanation. There is an interaction between the iron and the enamel when you have cobalt present; when you do not have cobalt present there is no interaction. Sample 1 (see illustration), which is enameled with the non-cobalt ground coat, is nicely covered; but under impact the enamel comes off, leaving the bright steel (see dish 3). Sample 2 is covered with the same enamel with 1 per cent. of oxide of cobalt added, and when subjected to the same blow, adheres firmly in ridges, barely exposing the steel between them (see dish 4). Samples Nos. 5 and 6 also show how the adhesiveness, under punishment by rapid changes of temperature, is promoted by the addition of oxide of cobalt. Both have been heated red hot and plunged into cold water. Number 5, whose fundamental coating contains no cobalt, peels off clean, to the steel, while 6, whose fundamental coating is the cobalt ground, exposes no steel at all.

Prof. Staley: I would like to have Mr. Landrum prove that there is an interaction between the ground coat and the iron when cobalt is present and no interaction when cobalt is absent. I would also like to see him demonstrate the presence of a porous alloy between the enamel and iron. In regard to what Prof. Purdy has said, I would like to know on what evidence he bases his statement that cobalt is merely suspended in the gound coat and, furthermore, to explain the mechanics of just *how* such a

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suspension, if it should exist, would make a more tenacious ground coat. We have one fact, namely, that the addition of cobalt to a ground coat for sheet steel enamels makes it a better ground coat. This is admirably shown by Mr. Landrum's paper. Beyond this one fact, we can merely speculate *until some one produces some evidence.*

Mr. Landrum: We are merely speculating as to the "mechanics" of the action of the cobalt, but I believe that these samples show to the naked eye that there *has* been an interaction between the steel and the cobalt-containing enamel, and that there *has not* been such an interaction in the case of the non-cobalt enamel. It might throw light on the subject to consider the fact that even a cobalt-containing ground coat will not adhere well to a steel surface unless that surface has been made rough, or porous or crystallized by pickling, sand-blasting, or annealing. It may be that the enamel simply sinks down into the pores of the steel, but the question is: Why should an enamel have to contain cobalt to do this? Now if some one has the facilities to make a cross-section of a piece of enameled steel, I would like to see it. Such a section might explain this matter.

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COBALT COLORS OTHER THAN BLUE.

By R. T. STULL and G. H. BALDWIN, Ceramic Laboratories, University of Illinois.

INTRODUCTION.

The color imparted to a glass or glaze depends upon the kind of coloring oxide, the composition of the batch and the manner of heat treatment. It has been considered that cobalt is persistent in producing blue under all conditions. Since two or more distinct colors are obtainable from all other coloring oxides under different conditions, there seemed to be no logical reason why some color other than blue could not be obtained from cobalt oxide.

Since cobalt oxide has so persistently given blue colors under normal ceramic practice, it was evident that a departure in composition must be made from the ordinary commercial types of glazes if a color different from blue was to be developed from cobalt oxide.

A speculation as to the possible colors obtainable from cobalt oxide as the sole colorant is of interest. Cobalt salts in solution under certain conditions impart pink, while under other conditions the color imparted is blue. It, therefore, seemed possible to develop all the different shades from blue on one hand to pink or even light red on the other. The problem was to develop a type of glaze that would bring out the pink or red color if such were possible, and the key to the situation was found in blowpipe analysis. Magnesia and magnesium minerals containing cobalt, when powdered, moistened with a solution of cobalt nitrate and heated, give a pink color. Alumina and alumina minerals containing cobalt, when similarly treated, give blue.

This suggested a glaze high in magnesia and free from alumina. It was recognized that if such colors could be produced they would be of greatest value for low temperature work. Since a high content of magnesia imparts refractoriness to a glaze, it would be necessary to introduce a "softener" which would not influence the color toward the blue. Of the two "softeners," PbO and B_2O_3, tried in a preliminary test,[1] it was found that the

[1] Vol. XII, Trans. A. C. S., pp. 707–708.

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former changed the magnesia-cobalt pink to blue, while the latter did not, hence B_2O_3 was selected as the "fluxing" or "softening" agent.

EXPERIMENTAL WORK.

First Group.—The first group of glazes was made in order to develop workable members over a range of temperatures. In this group the RO remained constant, the SiO_2 and B_2O_3 being variables. The limits covered were

$$\left.\begin{matrix} 0.2\ Na_2O \\ 0.6\ MgO \\ 0.2\ CoO \end{matrix}\right\} 0 \text{ to } 1.0\ B_2O_3,\ 1.0 \text{ to } 4.0\ SiO_2.$$

Twenty-four glazes were made in this group. The horizontal series are designated by letters and the vertical series by numbers (see charts). The formula and batch weights of the four corner glazes are:

	Formulae					Batch weights				
	Na_2O	MgO	CoO	B_2O_3	SiO_2	Na_2CO_3	$MgCO_3$	Co_2O_3	$B_2O_3.3H_2O$	Flint
A–1.....	0.2	0.6	0.2	0	1.0	212	504	165	..	600
A–6.....	0.2	0.6	0.2	1.0	1.0	212	504	165	1240	600
D–1.....	0.2	0.6	0.2	0	4.0	212	504	165	..	2400
D–6.....	0.2	0.6	0.2	1.0	4.0	212	504	165	1240	2400

The four batches were weighed, ground dry for one hour, fritted and ground to pass 120 mesh. The different members in the group were made by blending the four extremes according to their combining weights.

Since the glazes settled rapidly and caked, it was found necessary to employ a "colloid" in order to induce flotation for application and adhesion on drying. Glucose, dextrine and glue were tested. The best results were obtained with 4–5 per cent. glue. Such large quantities of either glucose or dextrine were required in order to produce free flotation that the glazes cracked and curled up on drying. With glue, however, a high degree of flotation was obtained, and the glazes dried without cracking.

The glazes were applied in a thick coat on 2″ porcelain discs previously burned to cone 11. Three burns of this group were made, *viz.*, cones 2, 4 and 7 (Charts 1, 2 and 3). At cone 2

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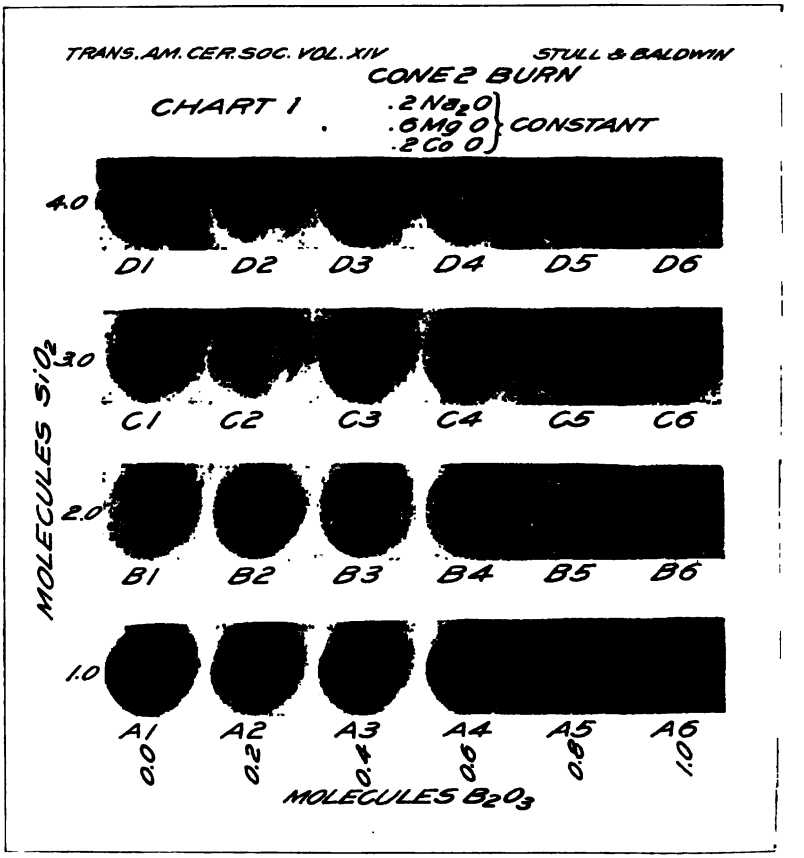

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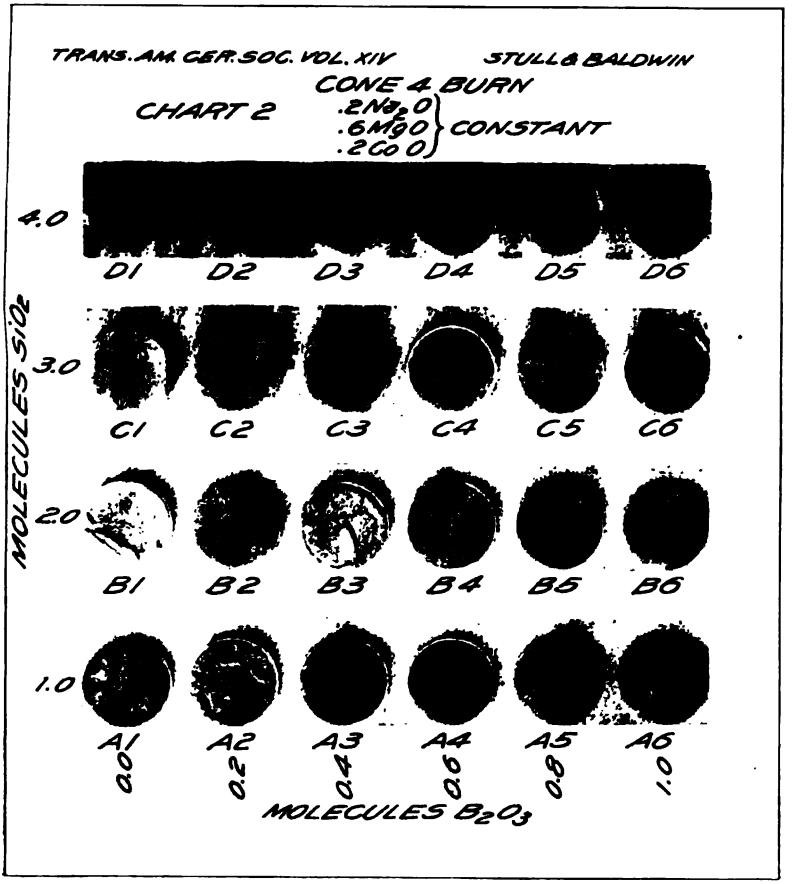

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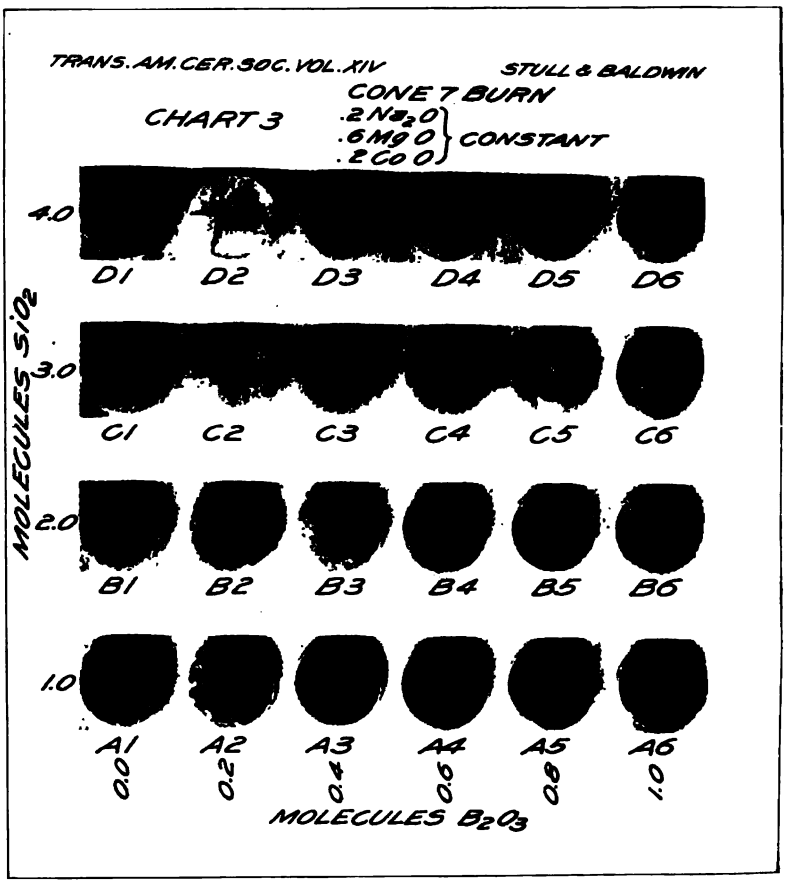

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(Chart 1) members C 6, B 5, B 6, A 5 and A 6 were well matured. A 4 and B 4 were well vitrified, presenting pleasing matte surfaces. Refractoriness increases on a line from A 6 to D 1. Member A 6 is a deep "red-violet" in color, showing more of the red than the blue. When we pass in any direction from A 6 upward or to the left, the red diminishes and the blue increases.

At cone 4 (Chart 2) the field of matured glazes has not materially broadened. A 4 and B 4 are still matte but their surfaces have changed from an "egg shell" texture to a promiscuously interlacing needle crystal, surface.

At cone 7 (Chart 3) the matured field has broadened only a little. A 5 and A 6 have reached a high state of fluidity, have flown down over the sides of the trials and are deep blue in color with a few spots of the red-violet here and there. These glazes show that they have attacked the body vigorously. In all three burns crystallization is quite prominent and brings out the red-violet color.

The results of this group indicate that a decrease in SiO_2 and an increase in B_2O_3 tends toward diminishing blue and increasing red, and that 2 molecules of SiO_2 as a maximum and 0.6 molecule of B_2O_3 as a minimum are the approximate limits in these directions for glazes that will mature well at or below cone 7.

Second Group.—A second group was constructed with the idea of bringing out more of the red and less of the blue and to develop glazes maturing at lower temperatures. This group, in which the constant RO is the same as in the first group, covered the following limits:

$$\left.\begin{matrix} 0.2\ Na_2O \\ 0.6\ MgO \\ 0.2\ CoO \end{matrix}\right\} 0.6 \text{ to } 1.4\ B_2O_3,\ 0.5 \text{ to } 1.5\ SiO_2$$

Twenty-five members were made, A 6 of the first group being stationed at the center and having the new nomenclature of G3. The members were blended from the four previously fritted extremes, the same as was done in the first group. The formulae and batch weights of the four extremes are:

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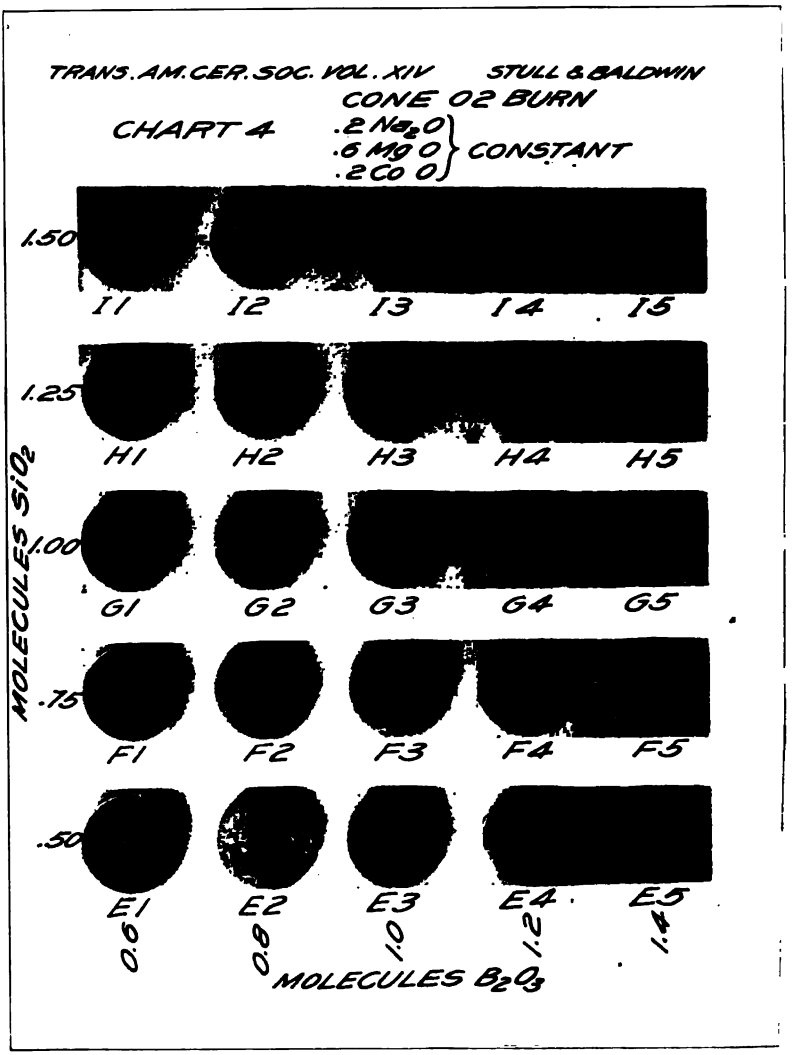

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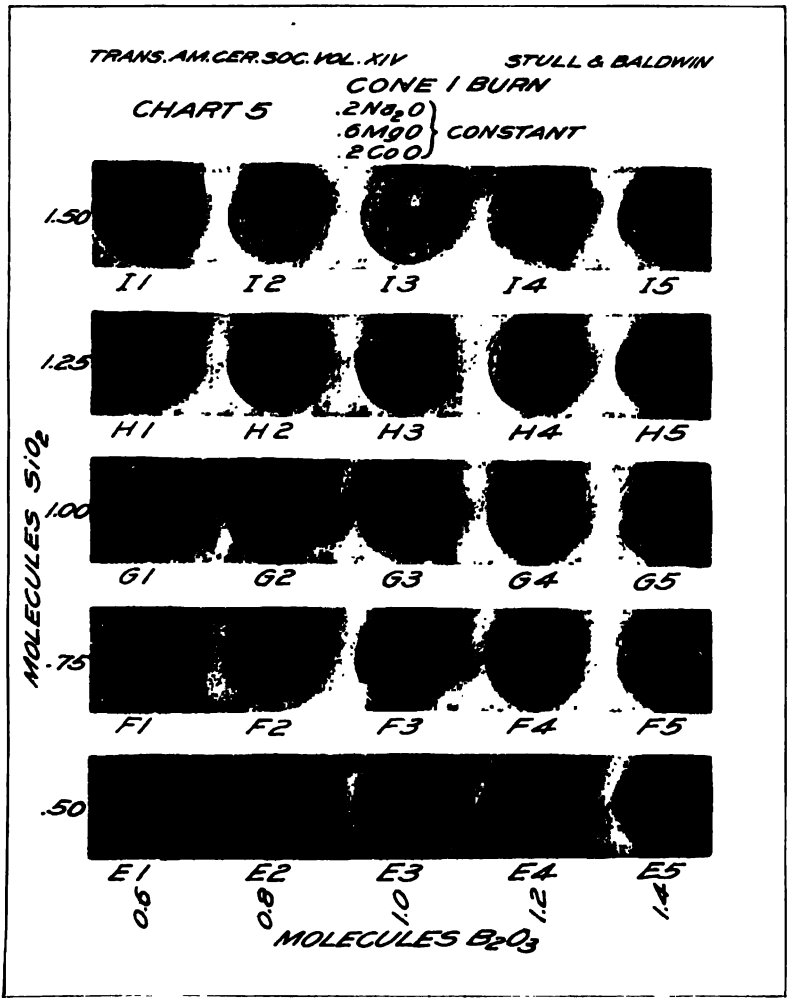

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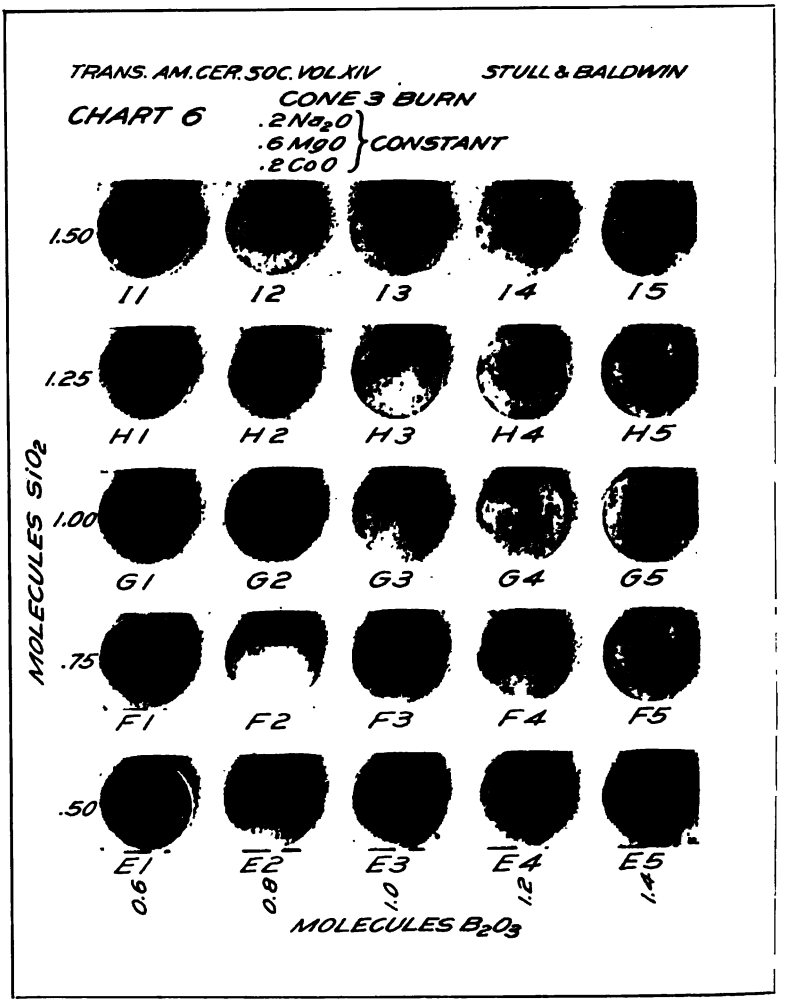

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	Formulae					Batch weights				
	Na_2O	MgO	CoO	B_2O_3	SiO_2	Na_2CO_3	$MgCO_3$	Co_2O_3	$B_2O_3.3H_2O$	Flint
E–1.....	0.2	0.6	0.2	0.6	0.5	212	504	165	744	300
E–5.....	0.2	0.6	0.2	1.4	0.5	212	504	165	1860	300
I–1.....	0.2	0.6	0.2	0.6	1.5	212	504	165	744	900
I–5.....	0.2	0.6	0.2	1.4	1.5	212	504	165	1860	900

Three burns were made, *viz.*, cones 02, 1 and 3 (Charts 4, 5 and 6). The red-violet color was well developed in all cases except in vertical series 1, containing 0.6 B_2O_3, which remained persistently matte in all three burns. Crystalline patches appear in all pieces where well matured. The red-violet color is more prominent where crystallization has taken place. Decreasing SiO_2 and increasing B_2O_3 tends to throw the color toward the red and away from the blue the same as observed in the first group. Where the glazes are overfired, they have "run" considerably, attacked the body and give a clear blue. Occasionally a small group of red-violet crystals appear in a clear blue field.

Several of the glazes in this group were applied to porcelain bisque vases. In all cases where the glazes did not flow excessively or where crystallization appeared, the red-violet color was prominent. Where excessive flow took place the glaze remaining on the surface of the vase was a clear blue. In several cases where the glaze flowed down over fire clay "buttons" used as setters, the color of the glaze on these buttons was a dark green. The best glazes in the group are E 3, E 4, E 5, F 3, F 4, F 5, G 3, G 4 and G 5. Member F 4 appeared to be the best one in all three burns.

Third Group.—A third group was made in order to obtain lighter shades of the red-violet color. Since F 4 seemed to hold the color so persistently and showed a fair range of temperature, it was selected as the starting point. Lighter shades can be produced by blending F 4 with a similar glaze but containing no cobalt oxide. The first problem to solve was to produce such a glaze having the same heat range and fusibility as F 4. In order to save time it was decided to make a triaxial group (Chart

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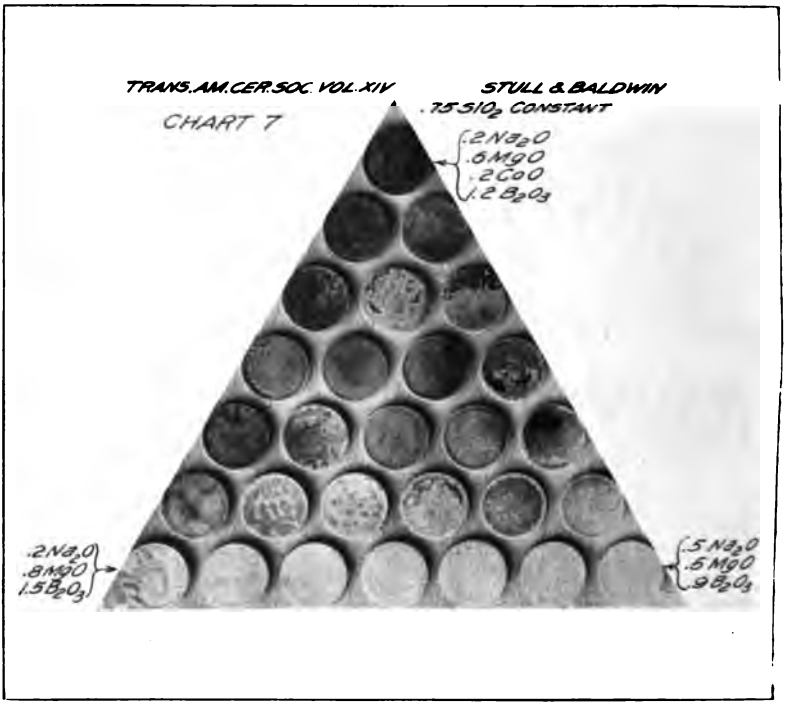

7) by placing F 4 at the upper apex, and the two following colorless glazes at the lower corners:

$$\left.\begin{matrix} 0.2\ Na_2O \\ 0.8\ MgO \end{matrix}\right\} 1.5\ B_2O_3\ 0.75\ SiO_2 \qquad \left.\begin{matrix} 0.5\ Na_2O \\ 0.5\ MgO \end{matrix}\right\} 0.9\ B_2O_3\ 0.75\ SiO_2$$

The only constant member in the group is SiO_2 at 0.75 molecule.

The group was made by fritting the three extremes and blending as was done in the two preceding groups. Glazes were applied to porcelain discs and burned to cone 02.

Examination of the trials indicates that there is no difference in shade or intensity of color from a content of 0.1 CoO to 0.2 CoO. The glaze near the lower left corner is a dark lavender while the one near the lower right corner is clear blue. As the MgO and B_2O_3 decrease and Na_2O increases, the color tends toward blue. Wherever crystallization appears, the red-violet or a lighter shade tending toward lavender appears.

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Purple Produced by Use of Cobalt

$$\left.\begin{matrix} 0.2\ Na_2O \\ 0.6\ Mg\ O \\ 0.2\ Co\ O \end{matrix}\right\} \begin{matrix} \text{G-5 at cone 0 2} \\ 1.4\ B_2O_3 \quad 1\ Si\ O_2 \end{matrix}$$

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CONCLUSIONS.

The color violet is composed of equal intensities of red and blue. Most of the colors produced in the foregoing work lie between the violet and the red. A fusion of either soda or boric oxide and cobalt oxide gives blue. Cobalt silicate is blue. A mixture of magnesia and cobalt oxide heated to redness gives pink. The color darkens tending toward red as the temperature of calcination is increased; the color change, however, is not pronounced until very high temperatures are reached.

The red-violet, lavender or pink color is apparently due to some combination of magnesia with an oxide of cobalt. Decreasing MgO or increasing SiO_2 causes diminishing red and increasing blue. This would indicate that the silica has broken up the magnesia-cobalt combination, thus imparting the cobalt-silica blue.

Although a fusion of B_2O_3 and CoO gives blue, an increase in B_2O_3 in the foregoing glazes tends toward the red and away from the blue, indicating that the magnesia-cobalt red-violet color is not only stable in the presence of B_2O_3 but that the latter encourages the red by some action not definitely understood.

DISCUSSION.

Mr. Wilder: I would like to ask what would be the result of increasing the heat in the trials shown on the last diagram?

Mr. Stull: You would tend to get less of the red-violet or lavender and more of the blue. This is probably due to the fact that the glaze becomes very fluid as the temperature increases and attacks the body vigorously. The alumina taken up changes the color to blue. We intend to continue further and try what we call an insulating glaze, by biscuiting the porcelain at 05 to 02, then applying a glaze similar to the first one on the board, as, for example:

$$\left.\begin{matrix} x\mathrm{Na_2O} \\ y\mathrm{MgO} \end{matrix}\right\} z\mathrm{SiO_2}$$

In this glaze x, y and z must necessarily be determined experimentally in order to fit working conditions. After applying the insulating glaze to the soft biscuit, the body is to be vitrified at cone 11 or cone 12, then the colored glaze is to be applied and

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burned to maturity. In this way we hope to exclude alumina from the glaze.

Mr. Wilder: I would like to ask Professor Stull if he ever tried to make pigments by calcining the magnesia?

Mr. Stull: No, I have never done that.

Mr. Landrum: I made pigments by calcining iron oxide with magnesia; but I never decided whether there was a compound formed or not, nor whether there was a red-violet color from the magnesia and the ignition simply gave a more homogeneous pigment. I think there should be some trials made by igniting at a little higher temperature.

Mr. Stull: If the color so obtained were stable, it would work all right, but apparently these colors are very unstable during fusion in the presence of silica and alumina. It seems to me that it would be possible to make over-glaze colors along this line, if they are not fired too high and thus made too fluid. The white sample in the right-hand lower corner of the triaxial is very fusible and has attacked the body vigorously as it is pitted in places. Therefore, the over-glaze colors would have to be fired with caution, or so constituted as to possess a wide heat range.

Mr. Will: I make blue stains of various composition which in cone 8 and cone 10 fire turn out a pink-violet, a beautiful color, but the invariable experience has been that on being used as colors under a full glaze they turn to a deep blue. In other words, the red color is not stable except with a matte glaze. For instance, use same as a stain for a matte glaze, or a semi-matte underfired, and you get a pink glaze. From this, purple glaze is often produced by overfiring, and on firing to a gloss the same piece will show a blue color.

Mr. Bruner: I would like to ask a question in regard to Chart 7. Professor Stull, do you wish to give us the impression that in the lower left-hand corner, the effect was due to low soda, high magnesia, high boric acid, and that if handled correctly, these glazes will give the pink color and on the other hand with low magnesia and low boric acid, the blue color comes out?

Mr. Stull: That is right.

Mr. Bruner: Are all those pieces exposed to just about the

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same heat or would you say their color was due to their position in the kiln? You do not mention anything about the fusibility and the possibility of the glazes being much more fused in one end of the kiln and the fact that when you have that condition it naturally leaves the color blue. On this piece (indicating number) you have a beautiful red-violet, as you call it, but inside it is blue. Even around the edges here you can see a little of the blue.

Mr. Stull: Underneath the red-violet glaze there is a thin film of blue next to the body, and where the glaze is thin the blue shows through. When crystallization takes place it brings out the red-violet color, and underfiring also brings out the characteristic red-violet color. On the inside of the piece, the thin glaze has attacked the body, thus giving the characteristic cobalt-alumina blue.

Mr. Will: I have applied one of these reddish blue colors to glazed Belleek ware and fired it again at glost kiln heat (cone 4–5) and there also one could not help noticing the phenomena of crystallization and the bringing out of red spots where underfired, while the balance of the piece showed a strong deep blue glaze with a high gloss.

Mr. Burt: I notice a number of these samples seem to show a distinct crystallization wherever the pink occurs, and I wondered whether Mr. Stull had examined it with that in mind. You get blue on the inside, but on the outer surface where you have sufficient surface glaze, you produce crystallization phenomena which develop this pink crystal. Is not the color something of a crystallization phenomenon?

Mr. Stull: It is true that the crystals do show the color, but the red-violet color is also developed in an underfired glaze and blue in an overfired glaze, or where the glaze is thin and has "fluxed into the body." On Chart 1, in the upper left-hand corner is the most refractory glaze in the group. It is as soft as chalk, yet it shows a light red-violet color. Alumina and cobalt together at a red heat will give a blue, while magnesia and cobalt will give pink. I do not know whether it is a chemical or a physical action that brings out the blue in one case and the pink in the other.

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NOTES ON THE PERFORMANCE OF A PRODUCER GAS-FIRED CONTINUOUS KILN.

By W. D. RICHARDSON.

I have been persuaded by the secretary to present to the Society some notes from my experience in the past year in operating the Youngren kiln. In doing this I do not presume to give any information to those who are using such kilns, but trust that a brief account of my struggles with this kiln may be of interest to many of our members who are considering or who will, at some time, consider the adoption of the producer gas-fired kiln. I should say in explanation that I had nothing to do with the installation or construction of the kiln, but took charge of the manufacture and sale of face brick of two factories at one of which, a stiff-mud plant, built about three years previous, the only kiln is a Youngren gas-fired kiln, the first one built, I think, for the burning of face brick exclusively.

The kiln, as constructed at this plant, and the local conditions affecting its operation will be briefly described.

KILN.

The outline drawings of the essential features of the kiln will make few words necessary to a clear understanding of it.

The kiln has 10 chambers, each 16 feet wide by 43 feet long, crowned by a half-circle arch, height, from floor to top of crown, 12 feet. The chambers are in one straight row, though the operation is continuous, chamber 1 being preheated by the hot gases passing from kiln 10 through the return flue A. It was planned to build a duplicate row of chambers parallel to this with a space between the rows of 25 to 30 feet and return the fires from 10 across this space and down the second row to 1, in the regular manner of continuous kiln operation.

The main gas flue B, a steel cylinder lined with fire brick, extends along the top of the kiln on one side wall and is connected by a portable sheet iron hood to the transverse distributing flues on the partition walls between the crowns of the chambers. From each distributing flue small flues extend down through the partition walls of chambers to the cross flues, in the partition

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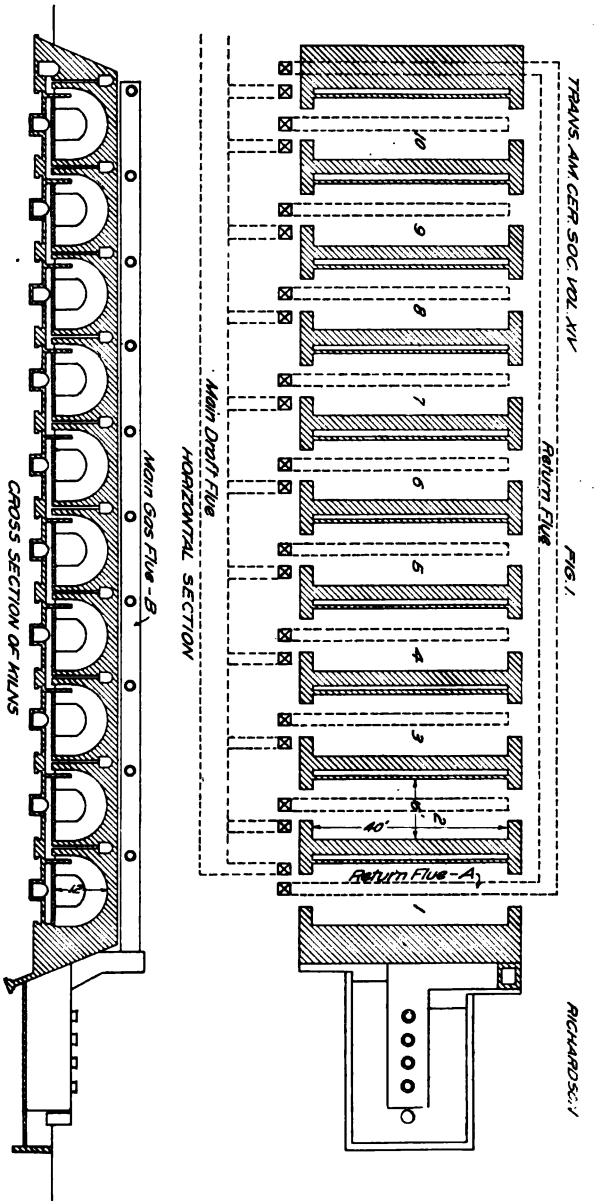

FIG. 1.

TRANS. AM. CER. SOC. VOL. XIV

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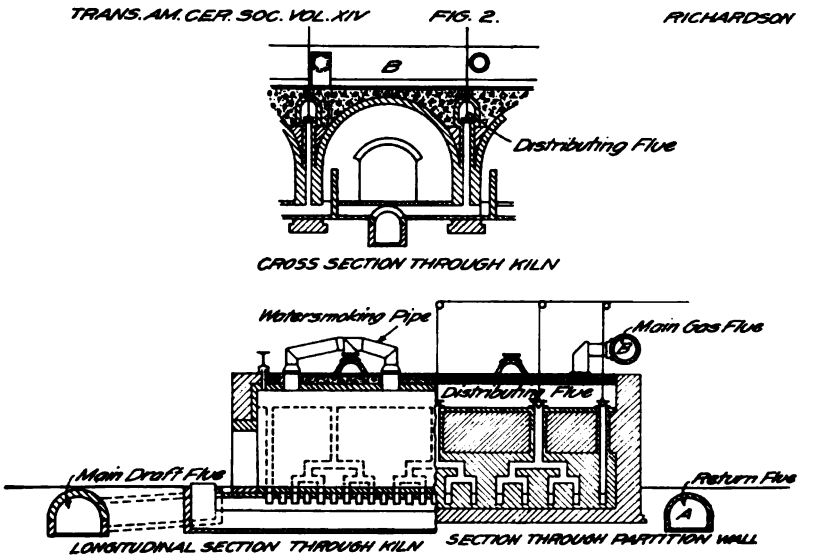

walls below the floor line, that connect the draft flues of the chamber behind to the bag walls of the chamber ahead. There are 14 of these cross connecting flues in a partition, each served by a gas flue in the top.

The end gas flues are straight and controlled by separate valves, but the other gas flues are branching, one valve controling 4 outlets These valves have rods extending up above the top of the kiln and are operated by means of wire ropes and pulleys, on one end of each chamber at the peep hole over the top of the bag wall, so that the burner regulates the supply of gas while watching the fires where they first come in contact with the ware.

The perforated floor flues have outlets also to an arched longitudinal flue, under the center of each chamber and extending out of one end, with provision for connecting with the main draft flue by means of a sheet iron breeching.

The main draft flue leads to a fan operated by an electric motor.

GAS PRODUCER.

The gas producer is a rectangular brick box or furnace, 7

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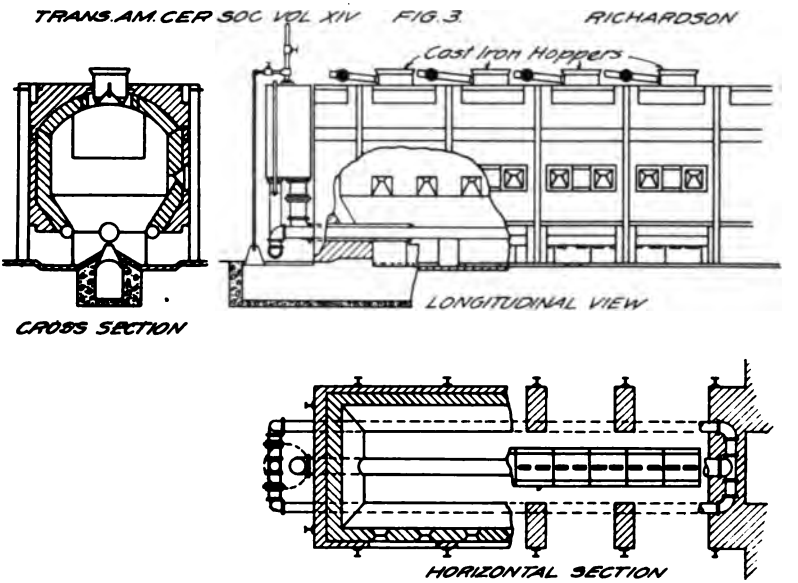

feet wide by 19 feet long, having in the top four circular openings provided with cast iron bell hoppers for charging with coal. There are no grates in the furnace and the ash outlets are covered with sheet iron. There is a row of poke holes at the level of the top of the fuel bed for the purpose of leveling the fuel bed after charging and for breaking down the clinker when cleaning out. For supplying steam to the producer there is a small vertical boiler at the front end of the producer connected with 3 pipes extending longitudinally through the hot-ash zone of the producer, so that the steam is generated by the waste heat in the ashes. These pipes, the center one 8″ in diameter and the side pipes 6″, are connected at the back end of the producer. Under the center pipe is a flue for the distribution of the air and steam. This flue has brick side walls and the top covered with V-shaped castings with opening under the pipe for the escape of air and steam above as shown in drawings.

The gas generated in the producer passes out of the back end into the soot chamber and thence into the vertical brick flue to which is connected the main gas flue previously described.

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CLAY AND PRODUCTS.

The clay used at this plant is a coal-measure plastic No. 2 fire clay, 6 to 8 feet being mined. The exact geological formation has not been definitely determined but it is about 100′ below No. 6 coal. The coal vein above the clay is only a thin seam, $^1/_4$″ to $^3/_4$″ thick, with no limestone above it.

This clay, or the central portion of it about 4 feet, is used at this factory for the making of a high-grade impervious, wire-cut face brick of a light buff, or yellowish white, color, at cone 2, running to a bluish white when burned to a higher temperature or held at a high temperature for a longer time. By mixture with manganese, gray brick are also produced at this factory.

FUEL.

The fuel used, No. 6 coal, is mined on the property by contract, from old workings left from operations 25 or 30 years ago, when a large coal business was done. This means that we get nothing but old pillars and stumps and coal near crop. We have no means of screening the coal, hence, though we aim to have the best of it selected for the producer, the miners get no extra pay for this and often give us considerable slack and some "bone" coal. The fireman picks out the "bone" coal and forks out the slack as far as practicable.

LABOR.

The operation of the kiln requires, for each 12-hour shift, a fireman for the gas producer and a burner to regulate the gas and air and manage the burning. The men employed for this during my management have been ordinary brickyard laborers of average intelligence, with but only a few months' experience in burning and in the operation of the gas producer. No expert service was available, and I had too many other matters in hand to give the kiln close attention.

CONTROLLING APPARATUS.

The kiln was equipped with draft gages, indicating and recording, and electric pyrometers, both indicating and recording. Draft and temperature charts were plotted in the little burners' house on one side of the kiln where the instruments were located in a glass covered case.

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THE OHIO MINING & MANUFACTURING CO.

RECORD OF BURNING

Chamber No. FACTORY No. 2 *Hole No.*——

Began Watersmoking at M

" Heating at M

" Firing at M

DATE	HOUR	MEASUREMENTS OF SETTLE
		FIRST MEASUREMENT
		1
		2
		3
		4
		5
		6
		7

Total Settle——inches

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There was no apparatus for analyzing the gas, nor for measuring its temperature at the producer. No regular measurements of settle were made.

I found that the burners were spending too much time in their house watching the instruments and not enough time at the kiln watching their fires. Moreover, I found the recording pyrometer and recording draft gage unreliable, so I discontinued their use. We continued the use of the inclined-tube, indicating draft-gage and of the long-stem thermometer in the watersmoking chambers. We also established a system of regular measurements and recording of settle every two hours. For this purpose I had cards made, that are tacked upon a board extending down from the roof to about 5 feet above the kiln. The measurement rod is a $^1/_2''$ pipe with a straight-edge iron tee welded on one end. The card is tacked on to the board with the rod in the hole and the upper edge of the tee on a line with the printed line marked "first measurement." At every succeeding measurement a line is drawn across the top of the tee with a pencil. The ruling is in eighths of an inch (see page 783).

DIFFICULTIES IN OPERATION.

Producer.—The difficulties arising in the operation of the gas producer are due, first, to the poor and variable character of the fuel, second, to the design of the producer itself and, third, to the lack of definite knowledge of the best manner of operating it as well as a lack of any means or apparatus as a guide in controlling the performance of the producer and maintaining it at its highest efficiency. Our only positive means of judging how well the producer is operating is by closely watching the burning of the gas in the kiln and the progress of the heating and burning of the ware. When the gas is burning well and proper progress is being made, nothing further is desired; but when the kiln is not heating properly and little or no progress is being made, the question is what is the cause of the trouble. Here is where experience and good judgment come into play. Action must be prompt, since, if much time is lost on a kiln with producer gas as fuel, no amount of effort thereafter can bring it up to the desired results. Every hour of delay or insufficient progress cools the

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chambers behind the fire, resulting in a lower temperature of air for combustion and a lower combustion temperature. When this cooling of ware behind has gone on to a certain degree, the kiln cannot be finished and nothing can be done but to move ahead to the next chamber.

So far as the inefficiency of the producer may be due to poor coal, we are for the most part helpless. We specify that our coal miners are to deliver the best of the coal to our producer, but sometimes in the old workings the best is not very good, and it is not to be expected that the men mining all coal at the same rate per ton will be as careful as we desire in the selection. Our burners throw out many lumps of slaty coal and try to keep out most of the slack. They know that too much slack will choke the producer and cut down its efficiency and increase the amount of labor.

Sometimes, undoubtedly, trouble is attributed to the coal when it is due to something else, possibly to the inefficiency of the operator, yet it is agreed by those who have had experience with gas producers that even for brick burning the best coal that is practically available should be used. It is true that the producer gas-fired continuous kiln makes possible the utilization of low-grade fuels such as lignites and peats for higher temperatures than are attainable with these fuels in direct firing, but those who are induced by promoters of this kiln to think that any grade of cheap fuel is practical for the gas producer are likely to be disappointed.

My experience indicates that a bituminous coal high in volatile matter is best for our use and the higher the temperature required for slagging the ash the less trouble experienced in the operation of the producer. Fine lump of uniform size is best; run-of-mine coal of good quality is practical, but requires considerable care in charging and leveling to prevent the formation of holes, and in consequence the producer running too hot and burning its own gas. I have not used any coal that did not require the addition of water to the gasifying air to prevent the slagging of the ash from cutting down the efficiency of the producer. I am willing to admit also that the proper amount of steam increases the thermal value of the gas, but I am not so sure

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that the quantity and distribution of the steam is so well regulated in our producer as to appreciably increase the heat obtained from the gas. But we know we cannot run our producer without steam as we must have the water for keeping down the temperature and preventing the ash from forming a molten slag and choking the producer. Steam is a convenient means, even in a suction producer, of drawing in the necessary air, and as the steam is generated by the heat of the ashes, the water pipes serve also to lower the temperature of the ashes.

The distribution of air and steam in this form of producer is uneven, due to the steam being admitted at one end of a flue having the slotted outlets varying in size from the obstructions of ash and clinker. This has a tendency, together with the unevenness in the size of the coal and in its distribution, to produce holes in the fuel bed. These irregular conditions lessen the efficiency of the producer.

The form and length of the producer being, with its four charging hoppers, practically four producers in one, with the gas from all passing out at the rear end, from the first three over one or more of the other holes in one producer caused by uneven operation or by the cleaning out of another, cause the burning of the gas in the producer, resulting in poor gas and a hot producer for sometime thereafter.

Just what should be the temperature of the gas leaving the producer I do not know, as I have never made any investigations of this. Vater says that it should be 850–900° F. If the producer is run too cool there is apt to be a deposition of tar in the flues, and if run too hot there will be trouble from soot caused by the breaking up of the hydrocarbons. Our producer is not capable of close regulation and is apt to run too hot.

The filling up of the soot chamber and the main gas flue with soot require the cleaning and burning out of these frequently, two or three times each round, and sometimes the outlets of the gas producers will nearly fill up with soot in a short time. The trouble is first noticed in the kiln, the heating up not progressing as it should; but this might be due to something else and an investigation and application of the remedy causes some delay.

All of these troubles with the gas producer can be over-

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come, or at least combatted successfully, by knowing what to do and doing it promptly. Experience, good judgment and activity are the essential requirements. Some change in the construction of the producer would overcome or lessen many of these troubles.

Kiln.—The difficulties in the operation of the kiln, outside of those arising from the producer are:

1. Choking up of the soot chamber and main gas flue with soot.
2. Choking of the small distributing gas flues with soot and tar.
3. Cracking of the walls of the gas flues, causing leakage of air into the flues or escape of gas into the kiln back of the ports.
4. Burning ahead too close—not enough chambers ahead or not enough behind the fire. Ten chambers not enough.
5. Difficulty of getting a good burn of the first chamber in the row, and a poor burn in one chamber always affects the next chamber adversely.
6. Difficulty of getting a hard burn on the end having the breeching connection to draft flue.
7. Interference with draft by suction from the chamber being set.
8. The swelling or increase in size of the hard-burned brick.
9. Repairs.

Only a brief explanation of these difficulties need be made.

1. The formation of soot is to a great extent a necessary evil. The greater the amount of volatile hydrocarbons and moisture in the coal, the greater the amount of soot formed. Undoubtedly also the maintenance of the proper temperature in top of the producer affects the formation of soot, as also does the height of the fuel bed. I have no definite data on this to present now. The burning out of the soot in our kiln causes considerable delay, the loss of one-half to one day every round. Moreover, with the imperfect arrangements for this, it can sometimes be done only by also drawing considerable heat from the chambers being burned.

2. The small flues that distribute the gas from the cross flues down to the 14 air flues are well adapted in this kiln to be choked with soot and tar. Only two of these flues are straight,

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one at each end of the chamber. The branching flues have horizontal parts where soot and tar can lodge. One valve for four flues would not, in any case, give uniform distribution; however, so long as the flues are all open and clean, the burning goes on satisfactorily; but when one or more of them get choked up, part of the kiln is falling behind and the burning cannot be finished unless the obstruction can be removed.

Sometimes these flues can be burned out so as to work properly again in an hour or less, and sometimes the obstruction either is not removed by the burning or soon fills up again, especially if the chambers behind have cooled so as not to sufficiently heat the air for combustion.

3. It was learned many years ago by the Germans that the placing of the gas flues between the crowns or in the partition walls gave trouble from the cracking of these flues due to expansion and contraction, and the plan was abandoned. This is not a very serious trouble with us, but is one thing to be looked after and is sometimes quite an annoyance.

4. Any one who has given much attention to continuous kilns knows that 10 chambers is not enough for satisfactory operation in burning brick to cone 2 to 4. In cool weather, when everything is running steadily, we get along very well as follows: four chambers behind the fire for heating air for combustion, one chamber under fire, two chambers preheating ahead of the fire, one chamber watersmoking, one being set, and one being emptied. But an extra holiday or anything causing a day's delay in setting, such as a break in manufacturing or, as frequently occurs in warm weather, a chamber too hot to empty at the right time, necessitates the holding back of the burning, the cooling of the air for combustion and underburned brick.

We aim to complete the burning of a chamber within 48 hours after putting the gas on it. If it runs much over 48 hours we cannot make any further progress with it and must move ahead. Forty-eight hours, however, is generally ample time for burning, as well as for setting and emptying a chamber. There should be at least 12 chambers, so that there could always be a chamber open for cooling ahead of the one being emptied and two chambers watersmoking.

5. A kiln with a single row of chambers, or what is called

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a semi-continuous kiln, is more difficult to burn than the full continuous kiln, since the conditions are different in the burning of every chamber, except three or four beyond the center, and systematic operation is practically impossible. In coming back to chamber 1, especially, the utmost care must be exercised in order to get even a fair burn, and sometimes we are obliged to give the kiln up half-burned and pass on, finishing the burning next round. When we start gas in the other chambers, the brick are incandescent all through the top and center and nearly through the bottom; but when 10 is burned and we are ready to start 1, the kiln only shows slight incandescence on the heads, just enough heat to start the burning of the gas. Therefore, often before this kiln can be burned, the air behind becomes too cool and further progress is stopped.

6. A periodical kiln having the draft connection at one end will burn harder at that end than at the other. But our Youngren kiln always has some soft brick at the end of the chamber having this draft connection. Of course the draft is not connected at this end during the firing, and the draft can have nothing to do with it. The only way that I can explain this result is that the opening through this end of the chamber, covered on the outside with an iron plate, conducts away so much heat to the atmosphere as to prevent this end from attaining as high a temperature as the other end. We know that this iron cover becomes very hot, so hot that if we were to cover it with sand it would warp the casting. The opening, 3 ft. square, is too large to cover with a fireclay slab. We have thought of making a reinforced clay cover. Such a cover would be heavy, but could be lifted with chain blocks.

7. The maintenance of the proper draft at all times is an important factor of successful results in continuous kiln burning. If there is leakage from the chamber being set into the chamber behind it, the draft will be short-circuited to some extent and interfere with the proper operation of the kiln. This will happen if the paper damper is not tight or if there are cracks in the brickwork. This would not bother us so much if we had more chambers in the kiln.

8. It has often been observed that when brick are burned hard on the top of a continuous kiln, whether gas-fired or coal-fired,

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they enlarge in size, while brick from the same clay burned in a periodical kiln will not have this defect. This may not be the case with all clays. This swelling or enlarging is generally attributed to the generation of sulphurous gases, not, in my opinion, so much from the sulphur in the coal as from sulphur in the clay, since where this phenomenon has been most marked, in my observation, the clay has contained considerable sulphur. But why is it that this defect is not produced in periodical kilns? It might be explained that in a continuous kiln where the sulphur gases from the fuel and from the clay pass from one chamber into another the ware must be subject to an atmosphere having a higher content of sulphur than in a periodical kiln, and though the brick may not have absorbed sulphur, yet the volatilization of the sulphur compounds in the clay would be delayed in such an atmosphere. We know that a portion of the sulphur is not driven off until a high temperature is reached and that this enlargement of the bricks does not take place until the last hours of the firing. In a continuous kiln, undoubtedly the conditions would favor a retarding of this action. A strong draft on the kiln seems to relieve this trouble.

9. Kiln repairs are generally a considerable item of expense at any brick plant where high temperatures are employed. The repairs on the Youngren kiln are little more than on any one-side firing, compartment kiln. Any one who has operated such a kiln at high temperatures knows that the partition wall and crown on the side of the chamber that is fired becomes much hotter than the other side and gradually pull toward the fire. The arch, coming down, pushes the other side up or over until finally the crown, or a portion of it, falls into the kiln or becomes so dangerous that it must be removed and rebuilt. Since I have been in charge of this plant, I have been obliged to rebuild the crown of every chamber—an expense of over four thousand dollars. It should be said that this was done about three years after the kiln was built. The cost of doing this is greater with the Youngren than other kilns, since the transverse gas flue between the crowns must also come down and be rebuilt. Beyond this the repairs on the Youngren kiln are no greater than on any other one-side firing, continuous, compartment kiln, except the repairs to gas producer. The repairs to gas producer should be a small item.

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With us the use of water in the boiler that is somewhat dirty at times forms a sediment in the pipes that burns them out. This is an expense of about $25.00 a year. The bottoms of the bell hoppers also burn out from improper operation of the producer. This is an expense of about $10.00 a year.

Repairs on a continuous kiln are more expensive than the actual cost shows, since the making of these repairs sometimes shuts down the whole plant.

CONCLUSIONS.

It may be interesting after having said so much to give my opinion of the gas-fired continuous kiln.

1. This type of kiln is the best that I have ever used for the burning of face brick (not flashed). It is an unnecessarily expensive kiln for the burning of cheaper wares, such as common brick, drain tile, paving brick, etc., though if used for such products the annular form should be adopted, instead of the compartment form. The form in any case should be modified to suit the products to be burned and other local conditions and could thus be adopted to various wares, such as roofing tiles, fire brick and, perhaps, some glazed goods.

The saving in fuel is not an important matter with us as compared with saving in labor and better results, since our coal costs us a little less than a dollar a ton in our hoppers. The coal delivered to our producer as well as to our periodical kilns and boilers is all weighed. Our Youngren kiln requires about one-half as much coal per 1000 brick burned as our round and rectangular downdraft kilns.

2. I have not seen the Youngren patent specifications and do not know what claims were allowed. I suppose that this special feature is the method of distributing the gas and controlling it. Similar methods have been employed in Germany, but not the same in every detail. For kilns with very long chambers some such method seems necessary, but the German method of underground distribution is, I believe, better in most cases. Gas flues on top of the kiln and in the partition walls are objectionable.

I do not know that the gas producer on this kiln was designed by Youngren. In any case it can be improved, and I believe that there are better producers on the market.

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NOTE ON THE DISSOCIATION OF CALCIUM HYDRATE.

By R. K. HURSH.

INTRODUCTION.

The present study, which was intended to be of a technological rather than of physical-chemical nature, was undertaken with the purpose of learning more regarding the properties and behavior of the compound $Ca(OH)_2$. The work has a practical bearing in demonstrating the value of methods of thermal study upon problems dealing with the dehydration of limes, cements and plasters.

A number of values have been given for the dissociation temperature of calcium hydrate. Herzfeld[1] says that dissociation evidently begins at 470° to 500° C. He gives the thermal effect of slaking CaO as 1.51 cals. per gram of $Ca(OH)_2$ and the maximum temperature of formation as 468°. H. Rose[2] found that pure calcium hydrate lost nothing at 100° C., absorbed CO_2 at 200° and 300°, and began to lose H_2O at about 400° C.

Le Chatelier[3] gives a vapor tension of 100 mm. at 350° C., and 760 mm. at 450° C.

Tichborne[4] found the precipitate from a heated solution of lime water to show a loss on blasting that corresponded to the formula $3CaO.2H_2O$. Others using similar methods failed to find such a hydrate.

Dr. Johnston,[5] whose work is taken up further on, found the dissociation pressure of $Ca(OH)_2$ to reach 760 mm. at 547° C.

METHODS AVAILABLE.

There are several methods of studying the dissociation of hydrates, such as the making use of heating curves, the determination of the aqueous pressure in direct or differential tensimeters, and the method depending upon the determination of the loss of weight at different temperatures.

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[1] Handbuch der anorg. Chem., C. Dammer.
[2] Pogg. Ann. du Physik u. Chem., LXXXVI, 105.
[3] Handbuch der anorg. Chem., 22, Gmelin-Kraut.
[4] Chemical News, XXIV, 199.
[5] Ztschr. phys. Chem., LXII, 330.

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HEATING CURVE METHOD.

A portion of the substance is placed in a furnace with a thermocouple touching it and another near it. The furnace is heated, and the temperatures of the furnace and substance are noted. At the point where dissociation takes place, a lag may be noted in the heating curve due to the endothermic reaction, *i. e.*, the absorption of heat due to the expulsion of water. It is frequently difficult and sometimes impossible to determine the point by this means, owing to the small amount of heat required for the reaction of the slow rate of dissociation. Distinction may be made between mechanically held or dissolved water and chemically combined water. In the case of chemical water, the lag will occur abruptly at the temperature of dissociation. Mechanical or dissolved water will pass off gradually over a range of temperature, and the lag due to these is gradual, showing no abrupt break at a definite temperature.

In the use of heating curves, close regulation of the temperature is very necessary to get reliable results. There should be no fluctuations in the heating of the furnace. Three general methods may be followed in the heating:

Indiscriminate, in which no attention is given to the rate of the furnace curve, and only the lags in the heating curve of the substance are given attention.

Constant rate, in which the temperature of the furnace is raised at a uniform rate.

Constant difference, in which a uniform difference between furnace temperature and that of the material is maintained. This method is the best, although the most difficult one of the three. The constant rate method gives good points, but the lag will, in most cases, be sloped instead of horizontal.

AQUEOUS PRESSURES METHOD.

Van Bemmelen, in studying the dehydration of the silicic acid gel, placed his samples in desiccators containing various concentrations of H_2SO_4. Constant temperature was maintained, and the samples were kept in the desiccators for sufficient time to reach equilibrium under the various vapor tensions. By plotting the loss of weight curve for the several concentrations of H_2SO_4 or the corresponding vapor pressures, he was able to

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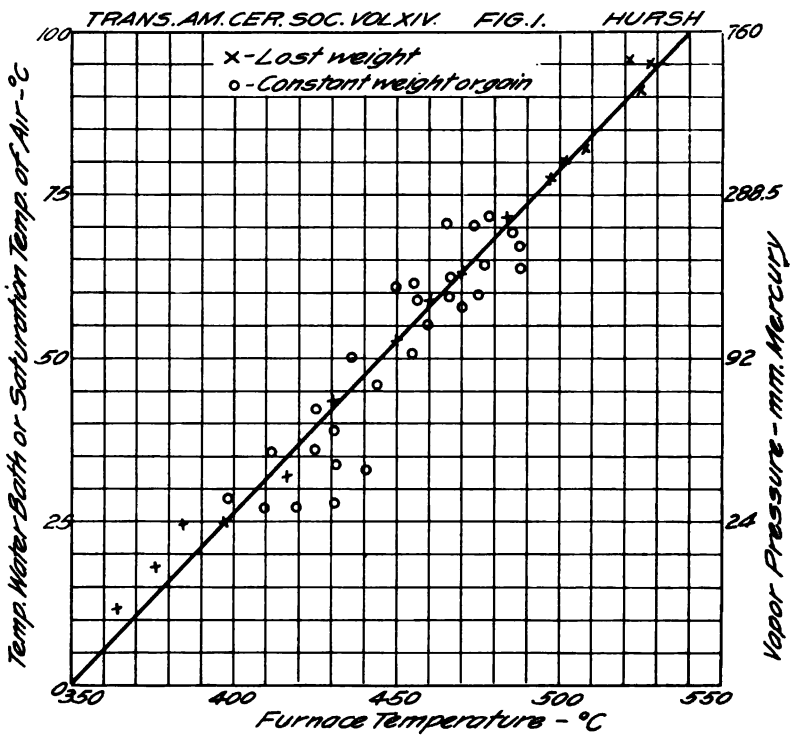
determine the inversion points and the degrees of hydration in each case. The same method has been applied by Prof. A. V. Bleininger[6] in studying the moisture in clays.

Dr. John Johnston[7] studied the dissociation pressures of several metal hydroxides and carbonates, using two experimental methods. The first was applied for hydroxides alone and is similar to one used by Brill. A small crucible containing a weighed portion (about 1.5 mg.) of the substance was suspended in a small electric furnace through which a current of air free from CO_2 and of definite vapor pressure was passed. The air was freed from CO_2 by passing through NaOH, then saturated with moisture by bubbling through a Liebig potash bulb, containing water, and



[6] Bulletin No. 7, Bureau of Standards.
[7] Ztschr. phys. Chem., LXII, p. 330.

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was heated before passing to the furnace to prevent any condensation. The temperature of the water in the Liebig bulb was regulated by immersing it in a water bath. The furnace was held at constant temperature, and the vapor tension maintained at a definite value for 10 minutes by regulation of the water bath temperature. The crucible was then removed from the furnace and weighed on a very fine balance. Conditions of temperature and vapor pressure were so regulated that the substance maintained constant weight or gained slightly during the period, and these values were taken as the corresponding temperature and dissociation pressure of the material. The results of this method for $Ca(OH)_2$ are shown in Fig. 1.

This method was found to be too slow and to frequently give inconsistent results. It was impossible to prevent the absorption of some CO_2 while removing the crucible from the furnace for weighing.

STATIC METHOD.

Dr. Johnston then resorted to the "static method," in which the dissociation pressures are measured directly. A diagram of the apparatus is shown in Fig. 2. A platinum tube, P, about 5 cm. long and 4 mm. inside diameter, contained the substance. This tube was placed in a small electric furnace with a thermocouple for determining the temperatures. A piece of glass tube, C, was fused to P and to one arm of a U tube which was connected to the barometer. On each arm of the U tube was a bulb, L, bent to the side and holding enough mercury to fill the U-tube to a depth of about 3 cm. To prevent condensation of the vapor from P, the U-tube and C were enclosed by a glass steam jacket.

With the mercury in bulb L, the apparatus was exhausted through A by means of a mercury pump. Cock A was then closed, and the mercury run from L into the U-tube by tilting the apparatus. Heating was begun, and at the first indication of pressure in P, the mercury in the two arms of the U-tube was brought to the same level by admitting some air at B and adjusting by means of the leveling tube R.

In his work with calcium hydroxide, Dr. Johnston slaked pure CaO and absorbed the excess water in a desiccator. Another portion was made by allowing the CaO to absorb moisture

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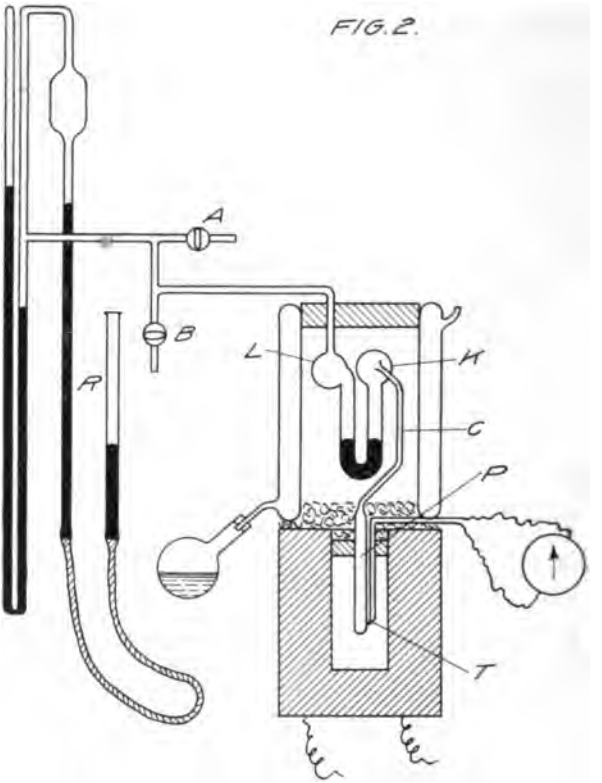
FIG. 2.



slowly until the composition was about CaO $0.8H_2O$. In using this substance, it was found necessary to heat it slightly during exhaustion of the apparatus since pressures of several cm. appeared between 200° and 300° which again disappeared in part on further heating. These abnormal pressures were supposedly due to loosely combined or absorbed moisture, and upon their appearance the test was stopped and the apparatus again exhausted. Only such pressures were taken as appeared at definite temperatures on heating and again disappeared on cooling. The "abnormal pressures" disappeared only partly on cooling. Under these conditions, it was found advisable to use a mixture of CaO and the hydroxide, although this did not entirely eliminate

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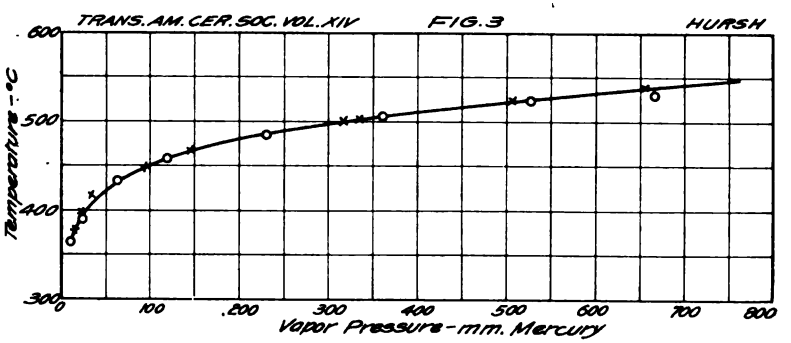
the trouble, which was noted with all of the hydroxides studied. The results of the work on $Ca(OH)_2$ by this method are shown in Fig. 3. By the curve, it is seen that the dissociation pressure



reaches 760 mm. at a temperature of 547° C. Hence this is taken as the dissociation temperature of the substance under atmospheric pressure.

In studying zeolites Friedel[8] heated them at successively higher temperatures in a current of air of approximately constant vapor pressure. This method was adopted by Allen and Clement[9] in their study of tremolite, using dry instead of moist air. A crucible containing the material was placed in an electric furnace, through which a current of air, dried by concentrated H_2SO_4, was passed. After heating for some time at a definite temperature, the crucible was quickly removed to a desiccator, cooled and weighed. Heating was continued at each temperature until practically constant weight was obtained. In one case, the experiment was repeated with moist air to determine the effect upon the results obtained by using dry air.

EXPERIMENTAL WORK.

This method was adopted for the present work. The hydrate was prepared by calcining pure $CaCO_3$ at 1050° C. and slaking the oxide with a slight excess of water. A portion of the hydrate was placed in a platinum crucible and heated in an

[8] Ztschr. phys. Chem., XXVI, p. 323.
[9] Am. Jour. Sci., Vol. XXVI, No. 152.

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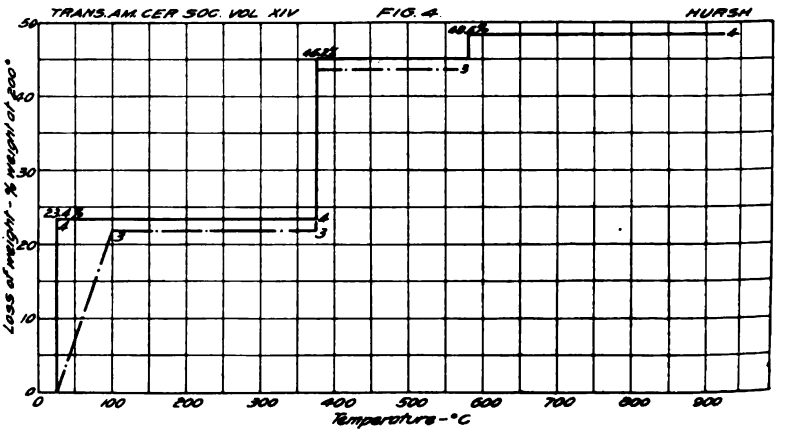
electric furnace in a bath of dry air, free from CO_2, at successive temperatures from 200° to 750° C. at 50° intervals. At 30-minute intervals, the crucible was removed from the furnace and cooled in a desiccator over concentrated H_2SO_4. The heating was continued at each temperature until constant weight was reached. It was impossible to prevent the absorption of some CO_2 during the transfer of the hot crucible from the furnace to the desiccator. The first loss of weight was noted at 400° C. Continued heating at this temperature gave a total loss of weight of 77 per cent. of the water present above 200° C. At 650° another loss of weight took place amounting to 22 per cent. A second trial was made with 10° intervals from 350° to 400° C., and the first loss was found to take place at 380° C.

To prevent the absorption of CO_2 by the sample, a method of weighing within the furnace was adopted. A platinum crucible was suspended in the furnace by a fine platinum wire from one pan of a balance that was carefully protected from unequal heating from the furnace. A thermocouple was placed with the junction just under the middle of the crucible. A current of air, free from CO_2 and dried by $CaCl_2$ and P_2O_5, was circulated through the furnace. A weighed portion of the hydrate was placed in the crucible and dried at 25° C. The temperature was then raised gradually until a loss of weight began at 375° C. It was somewhat surprising that there was no loss of weight be-



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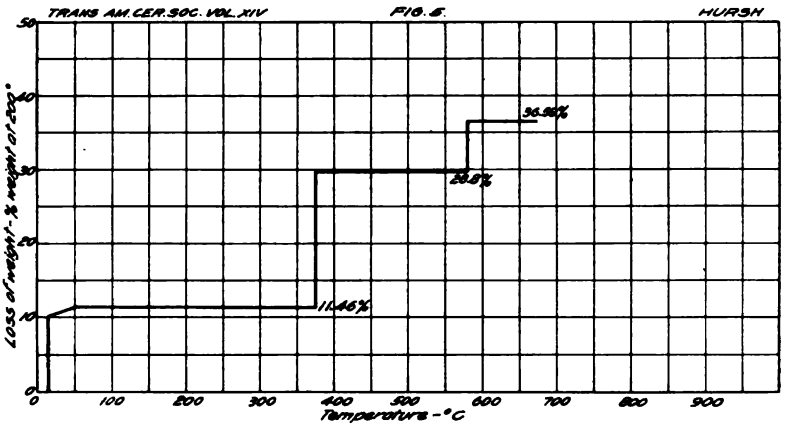
tween 25° and 375° as some mechanically held water might be expected. After constant weight was reached at 375°, the heating was continued beyond the point noted by Johnston. The second loss of weight took place at 580° C. The loss of weight curves for several trials are shown in Fig. 4.

To determine whether the presence of moisture in the furnace would have any effect upon the results, the air current was saturated at 0° to 1° C. before passing through the furnace, giving a vapor pressure of about 5 mm. The loss of weight was found to occur at the same points as before but to proceed at a slower rate. The quantitative results differ somewhat, due possibly to the longer time required in the latter trial. The result of the trial is shown in Fig. 5.



The results of these experiments indicate the existence of two hydrates of CaO, the $CaO.H_2O$ dissociating at 375° C., leaving a lower hydrate which dissociates at 580° C., leaving CaO. That the loss of weight at each point is due to the dissociation of a chemical compound is shown by the shape of the curves. The break is abrupt with no gradual slope preceding it. If mechanical or dissolved water were being driven off, there would be a gradual loss of weight with increasing temperature.

SUMMARY.

Various temperatures are given for the dissociation of $Ca(OH)_2$ ranging from 450° by Le Chatelier to 547° C. by Johnston.

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Using the "loss of weight" method, two dissociation points are found. The hydrate, $Ca(OH)_2$, dissociates at 375°, forming a lower hydrate that loses its H_2O at 580° C.

No mechanical water was driven off above 25° C.

In conclusion, the writer wishes to express his indebtedness to Professor A. V. Bleininger for many valued suggestions in this work.

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OIL AS A FUEL IN BURNING CERAMIC WARES.

By JOSEPH K. MOORE.

INTRODUCTION.

One of the most important factors in connection with the use of oil as a fuel in the ceramic industry is the source of supply. It is imperative in making a recommendation for the purchase of oil-burning apparatus to know not only that oil will burn the ware successfully, but that the price at which this oil can be obtained at the factory will not fluctuate over an area sufficient to wipe out any saving which an oil installation may make. It has been the experience of many firms that after the introduction of oil the price has been raised and the profit which was shown by their experiments was taken up by the increase in the market value of the new fuel.

Our first problem then was to find out how long a contract we could make, and what price per barrel we would be forced to pay for oil. After investigation, we found that it was possible to obtain a five-year contract at a price of 77 cents per barrel, delivered at the factory; hence, we had two known factors on which to figure our investment, the cost of oil and the period of time it was obtainable at this price. The next problems which presented themselves were: what type of burner to use, and how to obtain a successful salt glaze on our clay by the use of oil.

Other plants were using oil successfully, but the specific clay on which the subsequent experiments were made was difficult to glaze, and at the time the plant was first started, considerable difficulty had been experienced in procuring a coal which would glaze this ware in a satisfactory manner. It was found that by the use of some coals a very dull and unattractive glaze was procured, while with others a brilliant and heavy glaze was the result of firing. It was considered that sulphur was the agent destroying the glaze in this case. After numerous tests, however, a coal suitable to the clay was obtained, and the best results followed when lump coal was used early in the burn and lump and steam coal mixed when the heat reached 500°. The price of this coal was $4.80 for the lump and $3.71 for the steam; and though

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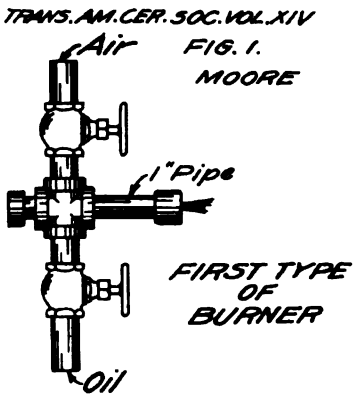
comparatively high, it was thought necessary since a coal with practically no sulphur was considered highly imperative.

EXPERIMENT I.

The Burner.—The first burner selected was the simplest that could be well imagined, and was constructed as per Fig. 1.



This burner had been formerly used on the plant for burning partition tile, where glazing was not necessary, and it was decided to try this type first.

The Burn.—Kiln A was chosen for the test, as it was one of the smallest on the plant. This kiln was set entirely with straight pipe, in order that the loss would be at a minimum in case the burn was unsuccessful. Trial pieces were placed near the wicket, about $^2/_3$ and $^1/_3$ of the distance from the bottom of the kiln. By the side of the test pieces were placed pyrometric cones, as is the usual custom in burning at this plant. The time-temperature curve was controlled by readings taken on a Le Chatelier pyrometer, placed in the wicket midway between the top and bottom of the kiln. The same burning schedule was followed as nearly as possible with the oil test as with the customary coal firing. There was no attempt made to get reducing conditions during the salting period, and six saltings were made at as frequent intervals as good practice would permit. The conditions under which Experiment I was made were not satisfactory, as the weather was rainy, which caused considerable difficulty,

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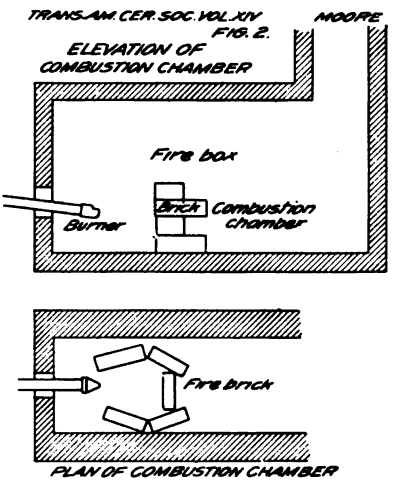
due to the water getting in with the oil, thus causing the burners to go out intermittently.

The result of the first burn was as follows:

Number 1 pipe	69.50%
Number 2 pipe	13.18%
Loss	17.32%

Glaze.—The glaze of this burn was much lighter than that procured by the use of coal; also, the glaze seemed to be thinner. From the standpoint of burning, this test was unsatisfactory, the percentages being very low; and the results, aside from the matter of cost, gave us very little encouragement. The fact of the burners giving out during the early stages of the burn developed a problem which had to be overcome, and it was found that by building a combustion chamber around the front of the burner and heating these brick to incandescence, the fires could be kept lit more continuously. We further found by studying the ware that the glaze could be improved to some extent by alternating oxidizing and reducing conditions during the glazing period. The construction of the combustion chamber is shown in Fig. 2.



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Fuel Costs.—The average cost of fuel for burning this kiln with coal, including the cost of hauling the coal to the kilns and carting away the ashes, was found to be $48.30.

Total oil used in Experiment I, 2,470 gal.

Cost of oil at 77 cents per bbl	$ 45.27	
Unloading, pumping and air, estimated	1.00	
	$ 46.27	$48.30
		46.27
Saving effected by use of oil		$ 2.03

Labor Costs.—

Coal system: head burner, per year		$1440.00
5½ men 365 days at $2.75		5520.63
Total		$6960.63
Oil system: head burner, per year		$1440.00
2 men 365 days at $2.75		2007.50
Total		$3447.50
Coal system per year	$6960.63	
Oil system per year	3447.50	
Difference per year	$3513.13	

ANOTHER TYPE OF BURNER.

After making Experiment I, although it was unsuccessful from a standpoint of the quality of the ware, we decided to investigate further and make several burns. At this time a company selling patented burners offered to equip one kiln for 30 days with their burners. For this reason it was decided to abandon the use of the first type of burner temporarily and avail ourselves of this company's offer. This burner will be referred to as "burner 2." Instead of using air for an atomizing agent, as in the case of Experiment I, steam was used in this burner. This burner belongs to the inside mixer class, which work on the principle that the steam and oil come in contact and the oil is atomized inside the burner itself. The mixer issues from the burner tip ready for combustion at once.

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Our experiments showed that after the burners had been on some time, and the kiln had reached about a red heat, no trouble was noticed from carbonizing, but this difficulty was experienced in the early stages of the burn, where it was necessary to keep a very low fire, hence, we were again compelled to resort to the use of a combustion chamber. Also, we found that we were more successful in atomizing with air at the lower, or watersmoking temperatures, than with the steam, but that after the temperature was raised, steam seemed to be the most efficient agent for atomization. After the first burn with burner 2, we cut in the air line on the early stages of the burn, and after the fire boxes warmed up turned on the steam.

EXPERIMENT II.

The Burn.—This experiment was conducted in the same manner as Experiment I, with the exception that the burner 2 and a somewhat larger kiln were used. Steam was used as the atomizing agent. As above mentioned, it was found that the steam did not work well in the early stage of the burn.

The percentages of this burn were as follows:

Number 1	88.64%
Number 2	3.33%
Loss	8.03%
Cost per burn	$54.75
Unloading, pumping, steam, air	2.00
	$56.75

Glaze.—The glaze on the ware showed an improvement over that of Experiment I, but it was still much inferior to that produced with coal.

FURTHER EXPERIMENTS.

Two more kilns were burned with burner 2. The average results and percentages were:

Number 1	92.03%
Number 2	3.39%
Loss	4.58%

The average cost of burning the kiln used in Experiment II

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and remaining experiments with coal, taking into consideration hauling the coal to the kiln and removing resulting ashes, was $76.15. Average oil used on kiln 8 for the last three experiments, 2,894 gallons.

Cost of same at 77 cents per bbl	$53.05
Unloading, pumping, steam, air	2.00
	$55.05

Saving effected by use of oil, $21.10.

Comparing burner 2 with our old burners, we secured the following:

Cost of oil, kiln 6, burn 221	46.27
Cost of coal, kiln 6, average	51.47
Saving	5.20
Saving, per cent	10.10%
Cost of oil, kiln 8, average of 3 burns	55.05
Cost of coal, kiln 8, average	76.15
Saving	21.10
Saving, per cent	27.70%
Increased saving with burner 2	17.60%

Glaze.—It was found that on the final experiments the glaze developed by alternating oxidizing and reducing conditions during the salting was of a waxy dark brown color, and not brilliant and glassy like that obtained by coal firing. The glaze seemed thicker than the coal glaze, and changed in character.

DESIGN OF BURNER EQUIPMENT AND COST.

The next problem was the cost of installation for a plant equipped with burner 2, as these showed a higher efficiency than the old type of burner. Fig. 3 shows a diagram of a plant with the piping and oil arrangement. Burner is used on Estimate 1. Estimate 2 is for old type of burner. The estimate includes three oil heaters and oil pumping outfit complete with individual oil meters for each kiln.

Oil Pumping Set.—This set consists of two $5^1/_4 \times 3^1/_2 \times 5$ Knowles duplex, brass fitted, steam pumps, mounted on cast iron trays, with heater and fitted with babbit rings in oil end (no fibrous packing required). This set is piped complete ready

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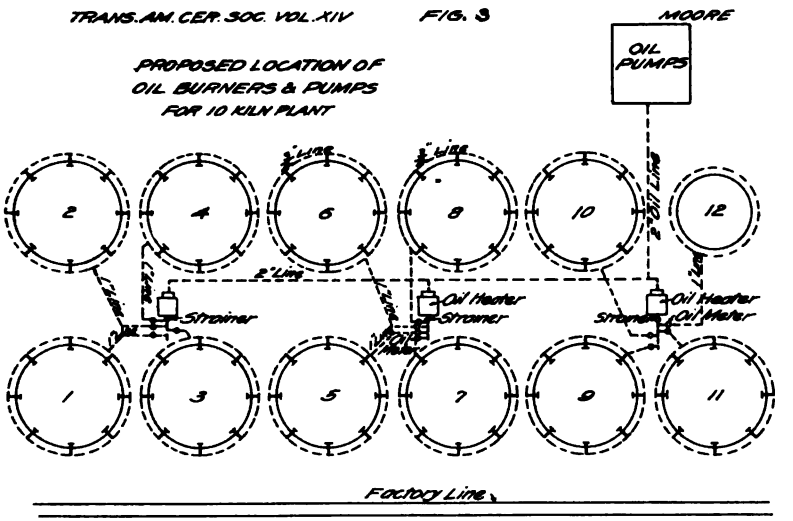

for operation, using Lunkenheimer regrinding valves and Kewanee unions throughout, and so arranged that either pump may be removed for repairs without interfering with the operation of the other. The set is equipped with the following accessories: 1" Witt pump governor; 1 pint Detroit sight feed lubricator; 30 gallon air chamber; 2" S. & P. self-cleaning oil strainer; thermometer; 5" pressure gauge; and 1½" American relief valve. The entire set is painted with black machinery paint and all brass parts polished. The oil heater furnished with this set is of the double pipe forced circulation type with connection in bottom for removing the water from the oil. This set is to be mounted on a concrete base.

Auxiliary Oil Heaters.—Three auxiliary oil heaters will be installed as shown in sketch, one for each group of four kilns. These heaters are to be of the same type as the heater furnished with the oil-pumping set but of a smaller size, and will be equipped with thermometers, pressure gauges, and 15 gallon air chambers to facilitate the removal of air and gas from the oil lines. Each heater is to be equipped with 1" S. & P. self-cleaning oil strainer. These are so arranged that the strainer may be cleaned without

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interrupting the flow of oil to the burner lines. Means are also provided for removing any water which may be in the oil.

Oil Meters.—The oil meters in the estimate are $12^5/_8$". $^3/_4$" Enarc oil meters, one for each kiln, each meter to be arranged with 1" main and by-pass valves and unions to facilitate their removal for inspection or repairs.

ESTIMATE 1.

			Total
Pipe 275'–$1^1/_2$"	@	7.30	$ 20.08
1250'–$1^1/_4$"	@	6.10	76.25
1250'–1"	@	4.50	56.25
900'–$^1/_2$"	@	2.60	23.40
Ells 45°			
94–$1^1/_4$"	@	0.11	10.34
94–1"	@	0.06	5.64
Ells 90°			
5–$1^1/_2$"	@	0.085	0.43
636–$^1/_2$"	@	0.025	15.90
Tees 106–$1^1/_4 \times 1^1/_4 \times ^1/_2$	@	0.22	23.32
106–$1 \times 1 \times ^1/_2$"	@	0.12	12.72
Reducers 94–$1^1/_4$—$^1/_2$"	@	0.12	11.28
94–1—$^1/_2$"	@	0.12	11.28
Valves 6–$1^1/_2$ globe	@	1.50	9.00
12–$1^1/_4$ globe	@	1.10	13.20
212–$^1/_2$ globe	@	0.43	91.16
12–1" globe	@	0.80	9.60
Heaters 3	@	70.00	210.00
Labor			250.00
Oil meters 12			110.00
Pumping outfit			420.00
Burners 94	@	30.00	2820.00
			$4199.85

ESTIMATE 2.

Old type burners 94	@	2.00	$ 188.00
Other items as above			1379.85
			$1567.85

GENERAL CONCLUSIONS.

First. Burner 2 showed 17.6 per cent. more efficiency than the old type of burners, but the old burners were not operated under the most favorable conditions.

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Second. It was determined to repeat experiments with the old type of burner under favorable conditions.

Third. It was found possible to glaze ware successfully by means of oil as a fuel.

Fourth. Oil-burning on this specific plant was found to possess the following advantages:

A. There is no cleaning of fires, no handling of fuel, no removal of ashes, no soot and dust.

B. It was found possible to reduce the number of men in the ratio of seven to two.

C. Oil could be stored in 50 per cent. of the space required for coal and 10 per cent. of the space required for cord wood of equal heating value, based on the following equality tables of western fuels.

EQUALITY OF FUELS.

Oil per bbl. at	Wood per cord at	Coal per ton at
$0.80 equals	$2.00 and	$2.80
0.85	2.15	3.00
0.90	2.25	3.15
0.95	2.36	3.32
1.00	2.50	3.50

$3\frac{1}{2}$ bbls. oil equals 1 ton coal; $2\frac{1}{2}$ bbls. oil equals 1 cord wood.

FUEL OIL.

Car.	Bbls.	Gals.	Wt. in Lbs.	Heat Units B. T. U.
1	238	10,000	79,000	1,461,500,000
	1	42	331.8	6,138,300
		1	79	146,150

APPROXIMATE HEAT UNITS (B. T. U.) PER POUND.

Oil.	Wood	Coal.
18,500	5,000	12,000

D. The ease and quickness of oil-firing over that of coal and wood showed a possibility of a more even control of temperatures, as shown on our burning curves.

E. Due to a more equal control of heat in each fire box, there seemed to be no localization of intense heat at one spot.

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F. The percentages seemed to increase with the knowledge of manipulation of the burners.

G. Due to the easy control of the burners, it was noted that oxidizing and reducing conditions in the fires could be produced at will, and change from one to the other could be obtained in shorter intervals than with coal.

H. It was further decided before any installation was made to experiment with other types of burners. These experiments we hope to report in a future paper.

In conclusion, the writer wishes to acknowledge and thank Mr. Raymond R. Smith for valuable work in conjunction with these experiments, and also the Western Clay Co., through their manager, Mr. Blain R. Smith, for the opportunity to do this work.

DISCUSSION WRITTEN AFTER READING THE PAPER.

Prof. Staley: The last conclusion is certainly a wise one. The principals underlying the proper construction of a good fuel oil burner to give any desired style of flame are so simple and the basic patents covering these principles have expired so long ago that there is little need to pay a large price for burners. This paper was submitted to the editor so late (July the 1st) that there was no time to secure or prepare adequate discussion. In a later volume I shall describe several types of home-made oil and gas burners and hope others with experience in this line will do the same.

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NOTE ON THE RELATION BETWEEN PREHEATING TEMPERATURE AND VOLUME SHRINKAGE.

By R. K. Hursh.

INTRODUCTION.

An extended study of the effect of preliminary heat treatment upon clays within a practical temperature range has been made by Professor Bleininger.[1] Especial attention was given to the effect upon the volume shrinkage. A decided change in the properties of most of the clays was noted at temperatures of 200° to 300° C. They became more or less granular and decreased markedly in plasticity. There was a material decrease in the volume shrinkage and an increase in the amount of pore water. In a few cases, this change occurred at somewhat higher temperatures. One fine-grained, highly plastic clay, similar in behavior to bentonite, showed a considerable change in physical properties at 250°; but treatment at temperatures up to 400° failed to reduce the shrinkage to working limits.

Professor Orton,[2] in studying some tertiary clays which gave trouble in drying, found ordinary preheating temperatures to be ineffective. When the temperature was raised to 450°–510° C. the plasticity and shrinkage were reduced sufficiently to make the clay workable. Under the conditions of the tests the period of safe treatment at these temperatures was closely limited since the clays lost their plasticity entirely when kept a little too long in the dryer. As some time is required for heat to penetrate the clay it is possible that the temperature may have reached a higher point in the longer treatments than was indicated by the thermo-couple. The test, however, represents the practical conditions in a rotary dryer.

EXPERIMENTAL WORK.

The present work was undertaken with the purpose of securing some further data upon the effect of the higher temperatures of preheating upon the physical properties of clays as indicated by changes in volume shrinkage. Four clays were used:

[1] Bull. No. 7, Bureau of Standards.
[2] Trans. A. C. S., Vol. XIII, p. 765.

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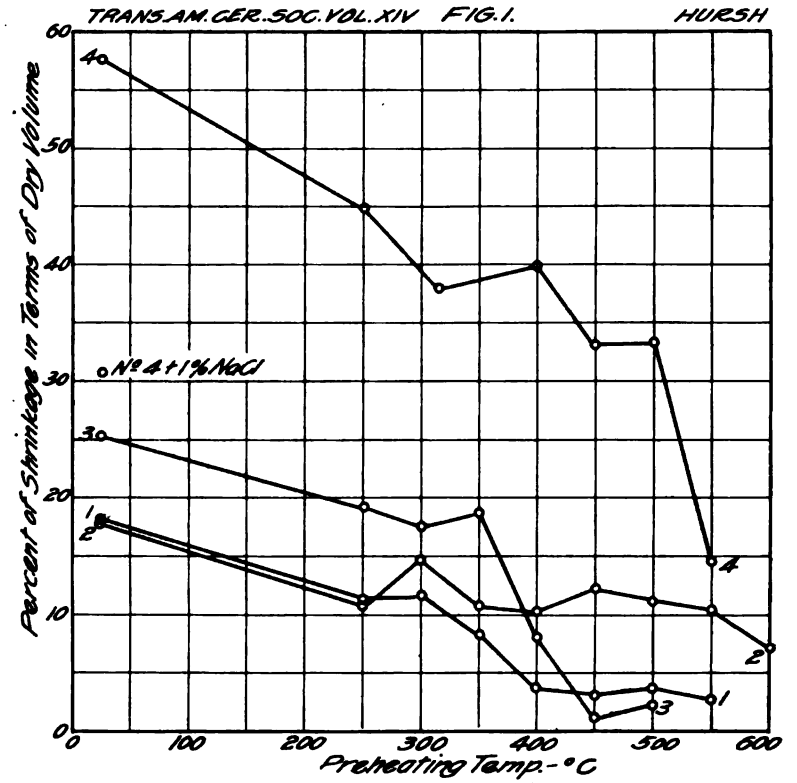
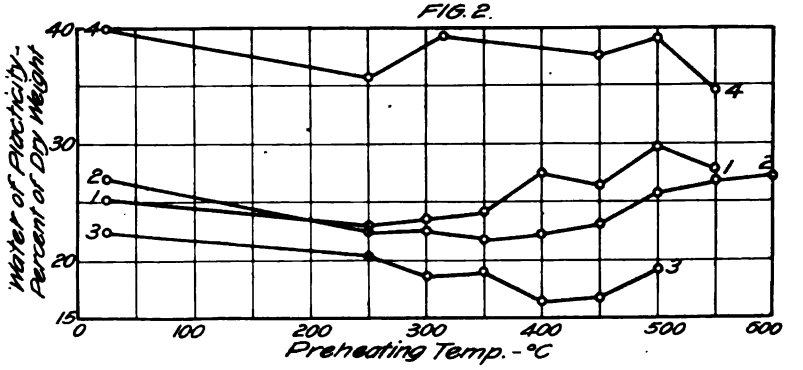


FIG. 2.



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No. 1. A plastic, somewhat sandy surface clay from Urbana, Illinois.

No. 2. A plastic, red-burning shale from Danville, Ill.

No. 3. A plastic, No. 2 fire clay, having a high drying shrinkage, from St. Louis, Mo.

No. 4. A fine grained, weathered shale from Saskatchewan similar in character to the clays studied by Professor Orton. It became very sticky in the plastic state and cracked to pieces under any conditions of drying. It is of interest to note that the addition of 1 per cent. of NaCl greatly improved the working properties and reduced the drying shrinkage nearly one-half. It would be possible by this treatment to make commercial use of the material.

The clays were heated at temperatures 50° apart from 250° to 650° C. for three hours, from 1 to 2 hours being required to reach the temperature. They were then ground to pass 20 mesh and made up into small briquets. These were weighed and the volumes measured, dried in air and at 110° in an oven, weighed, immersed in coal oil for several hours and the dry volumes measured. Care was taken to get about the same consistency in the samples when making up the briquets. The shrinkage curves are shown in Fig. 1 and the moisture content in Fig. 2.

DISCUSSION OF RESULTS.

The surface clay, No. 1, changed in color from yellow to brown at 250° and to a light salmon-red at 400°. The plasticity was considerably decreased at 250°, was very low at 400°, the briquets being very friable, and was entirely gone at 450°. The color changes seem to correspond closely to the changes in volume shrinkage. Above 300° the shrinkage decreased rapidly to 400°, beyond which the heat treatment had little effect.

The shale, No. 2, changed from gray to brown at 350° and to red at 400°. The plasticity was considerably decreased at 200°, but decreased gradually from 200° to 600°. At 650° no plasticity remained, and the briquets were too fragile to handle. The shrinkage decreases very little from 200° to 550° but drops considerably at 600°.

The fire clay, No. 3, decreased in plasticity gradually up to

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400°, but at 450° it became buff in color and was practically non-plastic. The effect of the heat treatment is much more marked than with the surface clay and the shale. The shrinkage curve drops very abruptly at 350°. The behavior of this clay is similar to that of an English ball clay studied by Professor Bleininger.[1]

The weathered shale, No. 4, changed in color from gray to deep maroon at 330°, at which point the cracking of the briquets was noticeably decreased but was still very bad. Cracking decreased gradually beyond this temperature, but the briquets at 550° were the only ones that remained sound with open-air drying. The sticky quality of the clay was retained up to 500°. At 550° it was quite granular but developed considerable plasticity with wedging. The effect of the heating treatment upon the shrinkage is more pronounced than with the other clays, but an abnormally high shrinkage remains 500°. Beyond this point the drop in the curve is so abrupt that very careful temperature control would be necessary in obtaining a sufficient reduction in shrinkage to prevent cracking without destroying the working properties. From the high temperature required and the narrow range of safe heat treatment, it is obvious that preheating would not be a safe method for practical use with such a clay.

The effect of the heat treatment upon these clays is quite different. The shale is most gradually affected, losing its plasticity entirely only at temperatures above red heat. It is probable that this is characteristic of the more homogeneous materials.

The fire clay shows an abrupt drop in its shrinkage curve, behaving similarly to other fire clays and a certain ball clay.

The fourth clay has such abnormally high shrinkage that only treatments above 500° C. would suffice to eliminate cracking in drying. It is evident that clays of this type are not adapted to preheating treatment.

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THE NOMENCLATURE OF CLAYS.

By Charles F. Binns.

Dr. Mellor has already published a paper[1] with the above title, and this contribution is made partly with the view of continuing the discussion and partly to assist in the discovery of a ground of agreement between ourselves and the ceramists of England. Dr. Mellor points out that "there is some confusion among the different writers on clays.....in the use of the terms clay substance, kaolin, china clay, and kaolinite," and he adds that "it is necessary for clear writing and clear thinking to assign as precise an unequivocal meaning as is possible to each of these terms."[2]

THE PRESENT CONFUSION.

In order to arrive at a clear understanding of the present uncertainty, a brief survey of the field will be made.

In the year 1867, S. W. Johnson and J. M. Blake[3] gave the name "Kaolinite" to a definite chemical compound occurring as six-sided, pearly scales. This was said to correspond to the formula

$$Al_2O_3\ 2SiO_2\ 2H_2O,$$

and was supposed to be the pure basis of, at least, white clays. The name was derived from the Chinese ideographs Kao Ling, meaning the lofty ridge and designating a locality where a pure clay was found. The word "Kaolin," from the same source, passed long ago into geologic and ceramic use, but the actual substance to which it refers has been differently defined by various authorities. Thus Ries[4] says: "When the mineral Kaolinite forms large masses the name Kaolin is applied to it." The same author says:[5] "This designation (Kaolin) should be restricted to white-burning, residual clays." Mellor[6] proposes to apply the term "Kaolin" as a generic term to the crude rock from which the China

[1] Transactions English Ceramic Society, Vol. VIII, p. 23.
[2] Ibid.
[3] American Journal of Science, Vol. XLIII, p. 351.
[4] "Clays of New Jersey," p. 47.
[5] "Clays, Occurrences, Properties and Uses," p. 8.
[6] Transactions English Ceramic Society, Vol. VIII, p. 27.

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clays of Cornwall are derived as well as to the clays themselves. Searle[7] objects to the name "Kaolin" as expressing location and not use. "Kaolinite." has been used to express the clay base theoretically corresponding to the Johnson and Blake formula, but not necessarily crystalline in form. Ries[8] says, "The most important (silicate) is the mineral Kaolinite, which probably occurs in all clays, and is termed the clay base or clay substance," and again,[9] "In any fire clay some of the silica is chemically combined with the alumina and water, forming a hydrous aluminum silicate, which for convenience of discussion we assume is Kaolinite," and adding as a footnote, "It probably is in most fire clays." Kaolinite in this sense is synonymous with Seger's "Ton-substanz," and with the English equivalent "clay substance."

Mellor[10] proposes to reserve the term Kaolinite to the rare crystal form of the mineral and suggests the name "clayite," giving Mr. Bernard Moore credit for the word, for the hydrous aluminum silicate which is not crystalline. He further refers the term "clay substance" to that part of clay which is decomposed by sulphuric acid, as in the Seger method of rational analysis. "Clay substance" also forms one of the divisions of mechanical analysis, being used to designate the sum of the particles less than 0.01 mm. in diameter.

"Ball clay" is also used in different ways. Potters will usually be found to refer it to a plastic, light-burning clay which has the property of easy vitrification, but Ries says:[11] "Refractoriness is desirable but those imported vitrify at cone 8, while the native ones require a much higher heat for vitrification."

It does not appear that special terms, outside the usual geological classification, are needed to define the colored clays which are used in the general manufacture of the heavier wares. It is, of course, sometimes necessary to describe the constitution of these clays, but in that case any definition of the constituent parts of white clays will apply.

[7] Note in Bourry's "Treatise on the Ceramic Industries," second edition, p. 50.
[8] "Clays, Occurrence, Properties, and Uses," p. 76.
[9] "Clays, Occurrence, Properties, and Uses," p. 206.
[10] Transactions English Ceramic Society, Vol. VIII, p. 28.
[11] "Clays, Occurrence, Properites and Uses," p. 204.

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For the sake of a clear argument, Mellor's summary is here quoted in full:

"Clay substance is a general term for those constituents of a clay which are decomposed by digestion with concentrated sulphuric acid, and the products of decomposition dissolved by alternate treatment with aqueous solutions of caustic potash and sulphuric acid. Clayite is a hydrated aluminum silicate which occurs in most clays in non-crystalline or amorphous granules. Analysis furnishes numbers corresponding with Al_2O_3, $2SiO_2$, $2H_2O$. Kaolinite is a variety of clayite which occurs in flat crystalline plates. China clay rock is a variety of disintegrated granite consisting of decomposed feldspar in the form of clayite, mica and quartz, with small quantities of other accessory minerals. China clay is a comparatively pure variety of clay, usually containing 95 to 99.8 per cent. of clayite. It is derived from china clay rock by natural or artificial levigation. Kaolin is a general term including both china clay and china clay rock."

SUGGESTIONS.

Among these definitions the present writer assents to only Kaolinit and china clay in their full meaning. Kaolin should mean only the natural deposit of a white-burning residual clay. This clay, when washed for market, may well be called china clay as Mellor suggests, but the term china clay rock is cumbersome and unnecessary. The fact that to the Chinese the word Kaolin meant both the crude and the prepared clay need not be seriously regarded. "Kaolinite" should be retained in its original signification of the mineral as defined by Johnson and Blake.

There remains, then, the clay substance or clay base. Mellor's definition of clay substance as that part of clay which is soluble in sulphuric acid is inadmissible because this fact has absolutely no significance in ceramic work. This has already been shown by the writer[12] in quotations from authorities. Neither can Mellor's suggested name "clayite" be allowed. This name has already been used of a mineral discovered in 1859 by J. A. and J. R. Clay, a sulphide of arsenic, antimony, lead, and copper.[13]

[12] Transactions A. C. S., Vol. VIII, p. 198.

[13] Dana, "A System of Mineralogy".

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Perhaps some will claim that it is not necessary to use any designation of the clay base because clay is clay anyway, and the amount of the hydrous aluminum silicate contained, say in a kaolin, is a matter of no importance. Even if this were not debatable ground, the fact remains that ceramic literature is full of expressions which are different, but which mean, and are intended to mean, the same thing.

The writer would be content with "clay substance" or "clay base," but if a name in mineralogical form be desired for what is not strictly a mineral it would not be difficult to find one. The chief objection to any such term is that the substance under consideration has no definite form or positive constitution. The existence of clay substance is only a convenient and workable theory, and it therefore should not be classed with minerals of established composition.

For the well known white clays found in Florida and Georgia some special name should be devised, though even between these there is a difference. Florida clay is washed and filter-pressed, while Georgia clay is sold without preparation other than the selection at the mine. Probably some qualification of the term "ball clay" would be best, such as "refractory ball clay," or "white ball clay." This, in the judgment of the writer, would be better than "plastic kaolin" as is sometimes used, because this term violates the definition already applied to kaolins. Obviously, the names derived from the states of Florida and Georgia are not satisfactory because these are not the only clays which these states produce.

These criticisms and suggestions are offered in order to assist in establishing an agreement upon the terms to be used in ceramic literature and discussion. It is certain that such an agreement is desirable and even necessary.

DISCUSSION.

Dr. Ries: I have listened to this paper with great interest, for the nomenclature of clays opens up a wide field for discussion. Many of us cannot avoid feeling that some of the names applied to clay are as meaningless as some of the terms applied to white ware.

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Several of the ideas expressed by Prof. Binns agree exactly with mine, as, for example, the loose manner in which the terms kaolinite and kaolin are used in the literature. There seems no reasonable excuse for this confusion. Kaolinite is a mineral name, belonging to the hydrous silicate of alumina having the formula Al_2O_3, $2SiO_2$, $2H_2O$. Kaolin, on the other hand, is a rock name, and refers to a white clay which may be made up wholly or in part of kaolinite. My personal preference is that the term kaolin should be restricted to the white-burning residual clays, which are similar in occurrence to the Chinese kaolin.

My objection to applying the same name to the North Carolina, Georgia, and Florida white clays is that they differ not only in their mode of occurrence, and consequently form an extent of deposit, but also in their physical characters. I have gone so far as to meet my opponents half way, and signified my willingness to call the Georgia and Florida white clays "plastic kaolins," for this will at least serve to distinguish them from the residual materials.

Another interesting point which has been brought up is the suggestion that kaolinite is the basis of most clays. As I have stated elsewhere at different times, we are not safe in saying this. Kaolinite may be, but there may also be other hydrous aluminum silicates, and in the high alumina clays we may have bauxite, or hydrargillite. Mr. S. L. Galpin, who has been investigating some of these high alumina clays in my laboratory, has found that many of them show appreciable amounts of alumina soluble in dilute sulphuric acid. Thus the "*aluminite*" clay, described by Greaves-Walker, from Kentucky had 21% of soluble alumina while the so-called halloysite from Alabama showed 10 per cent. Even the kaolins of North Carolina and Delaware may show 3 to 6 per cent. soluble alumina.

The term clay substance also needs accurate definition. I feel that it should be given a physical rather than a chemical or mineralogical meaning, in other words, that it should apply to the finest particles contained in the clay.

With regard to the hydrous aluminum silicates found in white clays, I believe that some of the terms now used, such as

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halloysite, are very indefinite and unsatisfactory, especially when their identity is based on non-crystalline materials.

The work of Mr. Galpin, already referred to, has brought out a number of interesting points which he will describe in detail in his paper. I may mention here, however, that even in some pure clays he finds relatively high amounts of such minerals as hydrargillite and muscovite, and only small quantities of kaolinite.

The term china clay, it seems to me, could be used broadly to include not only the white residual clays like those of North Carolina, but also the white sedimentary ones like those of Georgia and Florida.

The chemical analysis falls short as an accurate means of interpreting the mineral composition, for it is possible to have marked mineralogical variation without much change in the chemical composition. A white residual clay for example may contain as much as 20 per cent. muscovite, and yet not show enough variation from the composition of a high-grade kaolin to cause suspicion

Prof. Orton: I do not see why we can not sufficiently distinguish between the so-called plastic kaolin type, as represented by the bedded white clays of Georgia and Florida, and the less plastic or non-plastic type, as represented by the dike clays of North Carolina, by using the old terms primary kaolins and secondary kaolins. In that sense the word kaolin would mean a naturally occurring rock, the chief mineral component of which corresponds closely in chemical composition to kaolinite. A *primary* kaolin would be one found on the site of its formation, or in situ. The Dillsboro beds are a case in point. A *secondary* kaolin would be one which had been removed from its original point of formation, by erosion and redeposition. The Florida deposits are transported beds and so are those of Central Georgia. These secondary beds are kaolins just as truly as the primary ones—in fact, as ores of kaolinite, they are often richer than the primary beds; but it seems to me they should be distinguished by general agreement from the North Carolina type, which is so very different in its working qualities. Why is not the use of the

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words primary and secondary a simple and satisfactory way of settling the matter?

Professor Parmelee: It seems to me that in our attempt to devise a satisfactory classification and suitable terminology, we find that there are at least two quite different interests to be considered. On one hand, we have the ceramic chemist, and on the other the geologist and mineralogist. Obviously their interests are not alike, and that raises the question whether our undertaking will be any more successful. The term kaolin typifies to the ceramic chemist a white-burning clay of low plasticity. He is only slightly interested in its mineralogical character or mode of occurrence. The geologist will naturally regard color and plasticity of lesser interest.

In the matter of "clay base" I believe that Professor Binns is quite right in stating that it has no real significance but is merely used as a matter of convenience. Kaolinite should be retained for that which it originally signified.

Dr. Ries' suggestion to use the term china clay to include kaolin commends itself to me and I would point out what he undoubtedly had in mind, namely, that other residual clays, not products of the disintegration of feldspathic rocks or not containing kaolinite, could be included under this head. Unfortunately this would leave us without a name for the material prepared for the market by washing. As a matter of convenience, some suitable name should be had for such a product. Professor Orton's suggestion of the use of the terms primary and secondary kaolins seems to be more consistent and less objectionable than "plastic kaolin."

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OBSERVATIONS ON THE EFFECT OF PRESSURE ON THE VITRIFICATION OF CLAY.

By LEMON PARKER, St. Louis, Mo.

INTRODUCTION.

In the construction of large furnaces for gas benches, and similar purposes, blocks of considerable size are used, which formerly were wholly of fireclay, but in later years are made of the same mixture employed in silica brick, *viz.*, quartz 97 per cent., and milk of lime 3 per cent. As is well known, quartz undergoes a marked expansion, beginning at red heat or a little above, and allowance must be made for this expansion when constructing a furnace or the walls will be pushed out of shape or buckstaves will be bent or broken or other damage ensue.

It has been the custom in many places to use heavy paper or straw-board between the joints of these blocks of silica, which on heating burn out slowly, leaving the way for its volume to be replaced by the increased volume of the silica block at the time they undergo volume change. There are objections to the use of paper, and the writer undertook an experiment, substituting a thin slab of a clay brick, thinking that this material would not disappear at any stage of the burn and that it would become soft enough to flow out under pressure so far as necessary to give relief to the structure.

EXPERIMENTAL WORK.

A small test kiln was constructed as shown in the accompanying drawing. It was braced by heavy railroad iron buckstaves and hog chains strongly enough to resist any expansion which the material under test could exert. From side to side of this furnace, in the zone of most intense temperature, there was built an expansion bridge consisting of a row of silica bricks, placed end to end and with the spaces between filled with thin slabs of well burnt clay. This structure, when finished, made a straight bar of silica brick with about ½ inch joints filled with split bricks of fire clay. The fire clay splits stuck out well on either side of the silica bricks, so that part of the fire clay was exposed to the

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full heat of the gases which filled the chamber, but were not subjected to pressure, while that part of the clay between the ends of the bricks was exposed to the expansion thrust of the silica brick, and was protected from direct contact with the gases or flames.

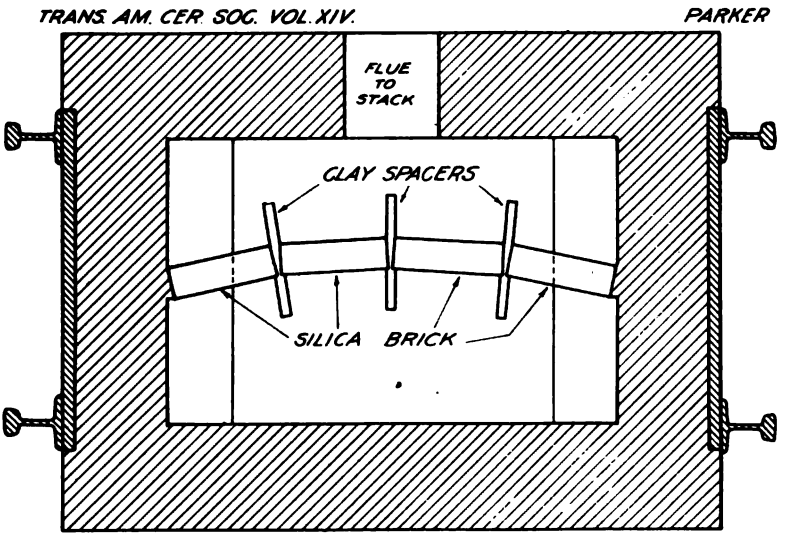

Fig. I.—Diagram of furnace.

The furnace was heated up by natural draft for 24 hours and then fired under blast for the high temperatures for 24 hours longer. The temperature of cone 25 was reached and held for 5 hours additional, without getting cone 26 down The silica brick had been burnt to cone 10 before use in this experiment.

The following measurements on the silica bricks composing the expansion bridge were recorded:

	Before test.	After test.
Silica brick No. 1.....	9 inches long	$9^{7}/_{32}$ inches long
Silica brick No. 2.....	9 inches long	$9^{3}/_{8}$ inches long
Silica brick No. 3.....	$8^{31}/_{32}$ inches long	$9^{11}/_{32}$ inches long
Silica brick No. 4.....	9 inches long	$9^{11}/_{32}$ inches long
Total length.....	$35^{31}/_{32}$ inches long	$37^{9}/_{32}$ inches long

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It will be observed that there was a gain of $1^{9}/_{32}$ inches in the collective length of four silica bricks from the heat treatment. To make this gain in length possible, one of three things must have happened: (*a*) The walls must have been forced apart. This was prevented by the heavy bracing. (*b*) The clay slabs between the silica bricks or the retaining walls must have either shrunk, or been compressed, or made to flow sufficiently to let the silica bricks expand. (*c*) The straight line of the column must have been deflected and the column formed into an arch. As a fact, both of the conditions described in (*b*) and (*c*) occurred. The resistance of the clay slabs was too great to enable the silica brick to expand wholly by compressing the clay bricks. Accordingly, the side walls were somewhat indented and the remaining distance was gained by the arching of the column and its deflection from a straight line.

The separating slabs of fire clay were burnt to cone 9 before use in this experiment. These slabs were ½ inch thick before the test. After the test they were deeply indented where under pressure, but not much affected where outside the line of pressure.

Fig. II.—One of the clay "spacers," sawed lengthwise so as to show the change in the body produced by compression.

The most notable thing to be seen from a study of the test pieces was the change of texture and color in the clay slabs where they had been under pressure. The ends of the slabs, which endured heat alone, were more or less porous, granular, and the original grains of the clays were still clearly marked. The color was a red-brown flash. Some grains could perhaps be detached, so little vitrified was the body. Between the silica brick, where the heavy pressure was exerted, the color had changed to a grayish blue or purplish blue, and the body had become dense and vitreous. The original grains were generally not identifiable and were absolutely non-separable. The two structures were

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so unlike that one would scarcely believe they were from the same clay, if shown the pieces separately.

CONCLUSIONS.

The writer desires to raise the question, What is the cause of this difference in color, in vitreous fracture, in density of body, in the same clay when treated at the same temperature. Is it the result of pressure alone, forcing the grains into such close contact that they could combine while they would not combine if separated by pores and voids in the unpressed portion, or is it due to the absorption by the clay bricks of silica from the silica brick at high temperatures, resulting in the formation of a more easily vitrifiable body, or is it due to the gases of the kiln not having equal access to the parts of the clay bricks under pressure and outside of the pressure line, and thus permitting reduction to occur in one place and not in the other?

DISCUSSION.

NOTE SUBMITTED AFTER READING THE PAPER.

Professor Orton: The stenographer failed to get any record of the discussion of this paper. It was discussed by Professor Havard, Professor Orton, Mr. Ellis Lovejoy, Mr. Parker, and several others. The consensus of opinion was that the marked difference in structure and color was due to the pressure under which vitrification had occurred A different opinion was voiced by one and concurred in by another, who explained the change on the theory that there had been an actual absorption of silica molecules from the silica brick by the clay brick during their enforced contact at high temperatures and that the alumina-silica ratio was thereby lowered and the clay thus rendered more fusible.

In order to check up this theory, analyses were made, by Professor Homer F. Staley at the request of the writer, of samples from the blue vitreous portion which had been under pressure and the yellow-brown porous portion which had not, and the silica was actually determined. It was found to be the same in both, within 0.24 per cent., which is inside the limits of probable variation in a roughly made brick. This disposes of the absorp-

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tion of silica theory, and leaves pressure as the probable chief factor in producing the remarkable difference in density and vitrification.

The writer believes that the blue color in the part under pressure may be attributable to two causes: (1) The density produced by pressure may have rendered the body practically impervious to gases, and therefore, unable to absorb oxygen in cooling and thus re-oxidize into the yellow-brown or "flashed" color, which the exposed porous portion readily did. (2) It is possible that the little understood reaction, known as "blue-stoning," *i. e.*, the change in color of a clay containing iron due to high heat under oxidizing conditions, may have occurred. This explanation seems less likely from the fact that the furnace was fired under blast for 24 hours and the gases were, therefore, probably strongly deoxidizing and blue-stoning would not be likely to occur in any portion of the mass, whether under pressure or not.

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THE EFFECT OF ACIDS AND ALKALIES UPON CLAY IN THE PLASTIC STATE.

A. V. BLEININGER AND C. E. FULTON, Urbana, Ill.

INTRODUCTION.

The effect of acids, alkalies and salts upon clay suspensions (slips) has been discussed frequently, and the work of Simonis, Mellor, Rieke, Boettcher, Ashley, Foerster and Bollenbach deals with the viscosity and other phenomena of systems in this state. But little is known concerning the effect of such reagents upon clays in the plastic condition which differs from that of a suspension, due to the cohesive influence of the particles upon each other.

It has been realized for some time that the properties of clays in the wet state are influenced by the presence of alkalies and acids. Seger explains the increase in the plasticity of clay upon storing by the assumption that the fermentation of organic substances results in acids which neutralize the alkalinity due to the decomposed feldspar, and in addition bring about the "sour" condition which accompanies the improvement in working qualities. Rohland[1] discusses this subject from the theoretical standpoint and makes quite definite statements with reference to the principles underlying the effect of various reagents upon clays in the plastic state. He arrives at the conclusion that the plasticity of clays is increased by the presence of H^+ ions, while, on the other hand, the OH′ ions are active in the opposite direction. According to Rohland, the plasticity is likewise increased by the addition of colloids like tannin, dextrine, etc., as has been shown by the work of Acheson, fine grinding and the storage of the clay in cool and moist places. It is supposed that the increase in plasticity is coincident with the coagulation which is primarily due to the presence of the hydrogen ions; it is retarded by the hydroxyl ions. The salts of strong bases and weak acids which dissociate OH′ ions hydrolytically produce an effect similar to that of the hydroxyl ions. Neutral salts, Rohland goes on to say, with but few exceptions, are indifferent in their

[1] "Die Tone," pp. 35–19.

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effect, though some appear to show a contradictory behavior, which has not yet been explained. "The effect of the hydroxyl ions may be weakened, compensated or strengthened by the action of the salt in question. Thus borax is an example of the first class and sodium carbonate of the second."

The same writer further says that with some clays the addition of Na_2CO_3 brings about an improvement in plasticity, while ordinarily the same reagent behaves in the opposite sense, due to the hydrolytic dissociation of OH' ions. It is possible that the effect of hydroxyl ions might be neutralized by the CO_3'' ions.

DRYING SHRINKAGE.

A decided lack of data exists with reference to the determination of the effect of reagents upon the plasticity of clays. It was thought advisable for this reason to begin work along this line without reference to any theoretical speculations. The most obvious criterion to be used in this connection is the drying shrinkage, which, from what we know of the properties of clays, is a function of plasticity. It is evident that any effect caused by the addition of reagents will at once be indicated by the shrinkage of the clay.

In this series of experiments Georgia kaolin was used. This clay was found to show an acid reaction when tested with phenolphthalein. This would indicate that the addition of acid should bring about no decided change in the clay, a fact which was verified by experiment. The reagents employed were HCl, H_2SO_4, NaOH and Na_2CO_3. In carrying out the work a thoroughly mixed sample was first prepared so that variations due to differences in composition were reduced to a minimum. The test specimens were in the shape of bars $3^5/_{16} \times 1 \times {}^5/_8$ inches. Even the most careful linear shrinkage measurements by means of the vernier caliper were found to be unsuitable for the work. A volumenometer permitting of readings to 0.05 cc. was then employed. The measuring liquid used was petroleum from which the lighter oils had been expelled by heating. The bars were at once weighed and allowed to dry at the laboratory temperature for three days, after which they were heated at 110° to constant

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weight, and their shrinkage determined. For each concentration of reagent three bars were made and measured.

Clay and Water.—A study was first made of the drying shrinkage of the clay with different amounts of water, ranging from the soft state in which the clay could be barely molded to the condition of minimum water content when molding was likewise difficult for the opposite reason. The shrinkage relations to the various contents of water are shown in Fig. 1. The third point on the curve, showing a shrinkage of 10.45 per cent. with a water content of 32.8 per cent., represents the most workable state. Any increase in water above this point is at once observed by the rapid softening of the mass. The clay hence is well suited for the work at hand, owing to the ease with which the condition of best working behavior is recognized in distinction from many other plastic clays which possess a long working range.

Effect of Acid.—Upon adding from 0.025 to 0.525 gram of hydrochloric acid to 100 grams of clay, we observe from Fig. 2 that the shrinkage is not materially affected by this reagent. While two maxima of somewhat greater contraction are noted, the principal result seems to be a reduction in shrinkage, contrary to what might be expected from Rohland's statements. The fact remains, however, that conditions are more complex than they seem, due to the probable solution of various salts in the clay as well as the formation of some chlorides by the acid.

It was thought that further insight into the effect of the acid might be obtained by calculating the total and the shrinkage water in terms of the true clay volume, *i. e.*, weight divided by the density of the powdered substance, according to the relation:

$$\frac{100\,(v_1 - v_2)}{\frac{w}{d}} = \text{per cent. (by volume) shrinkage water.}$$

Where v_1 = volume of wet brickette,
v_2 = volume of dry brickette,
w = weight of brickette, dried at 110° C.,
d = density of the dry and powdered clay.

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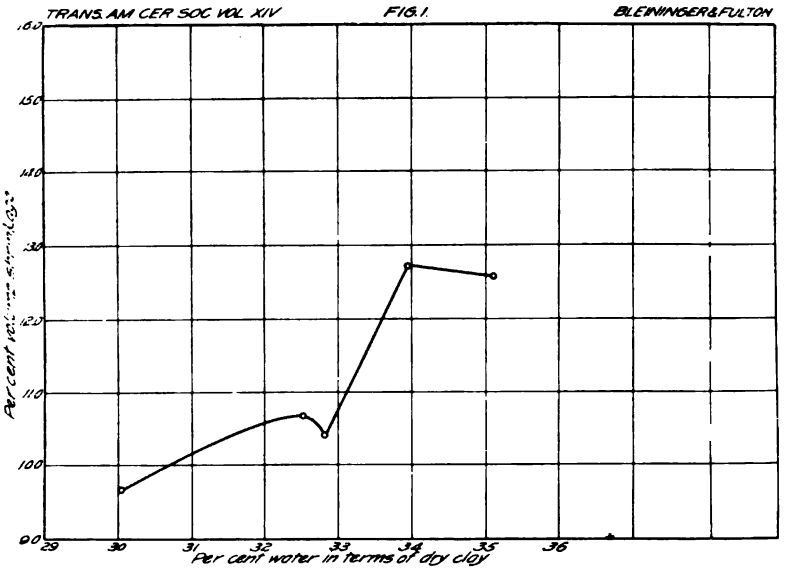

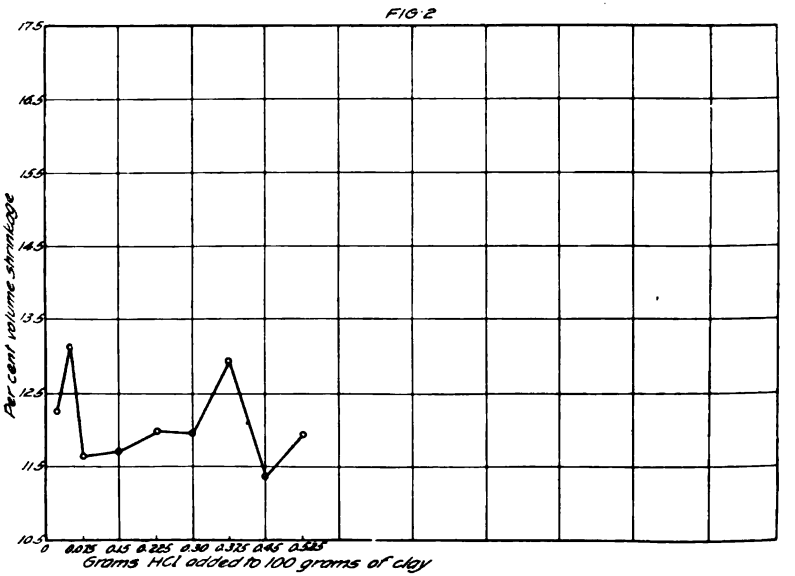

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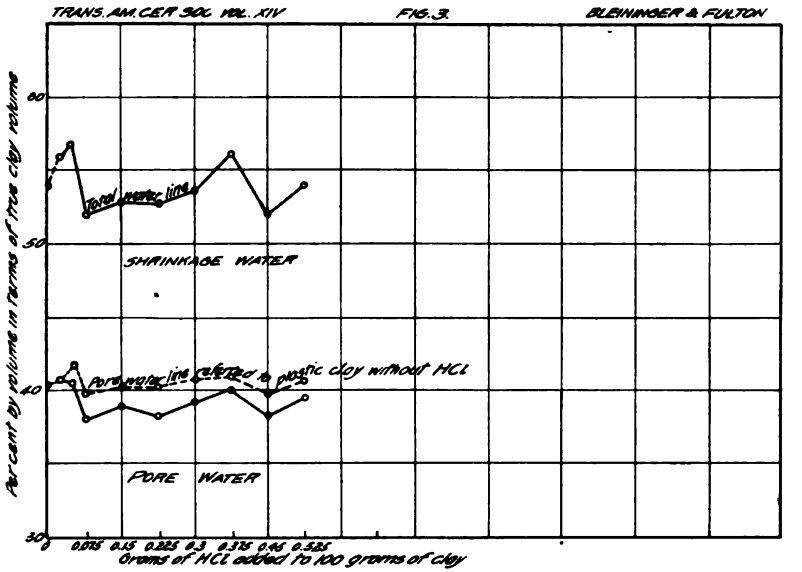

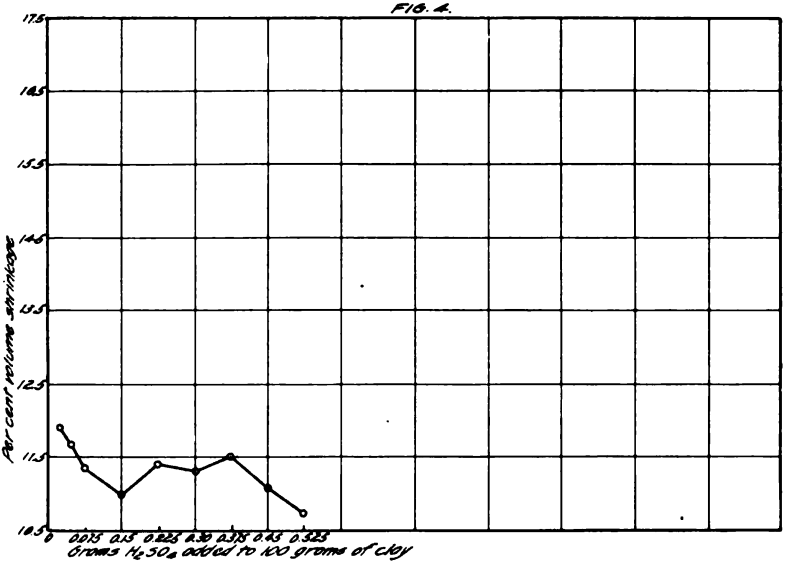

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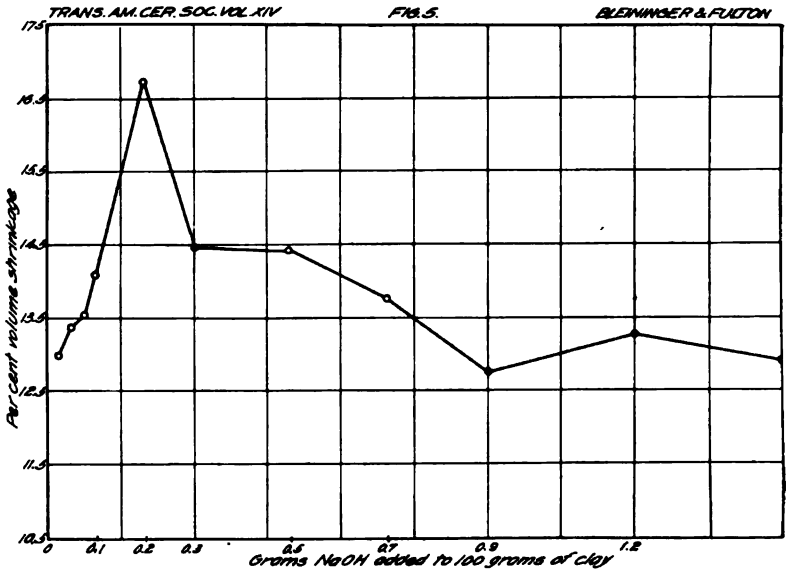

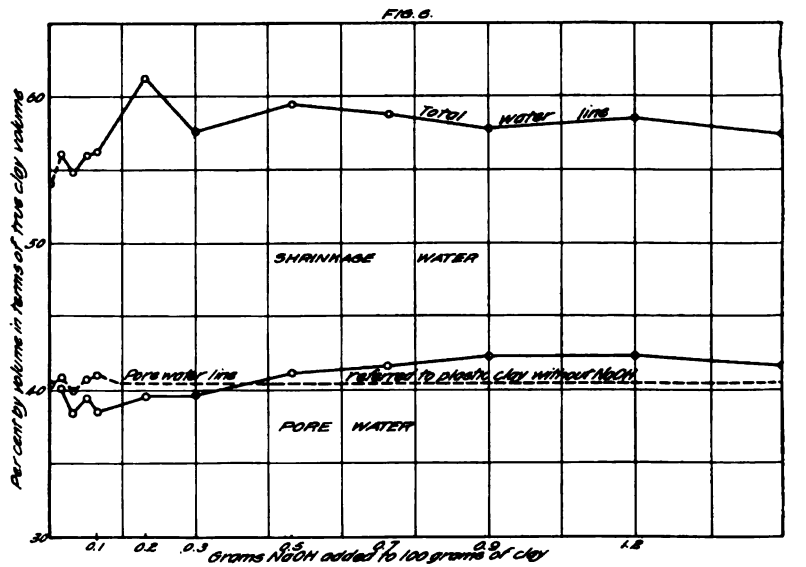

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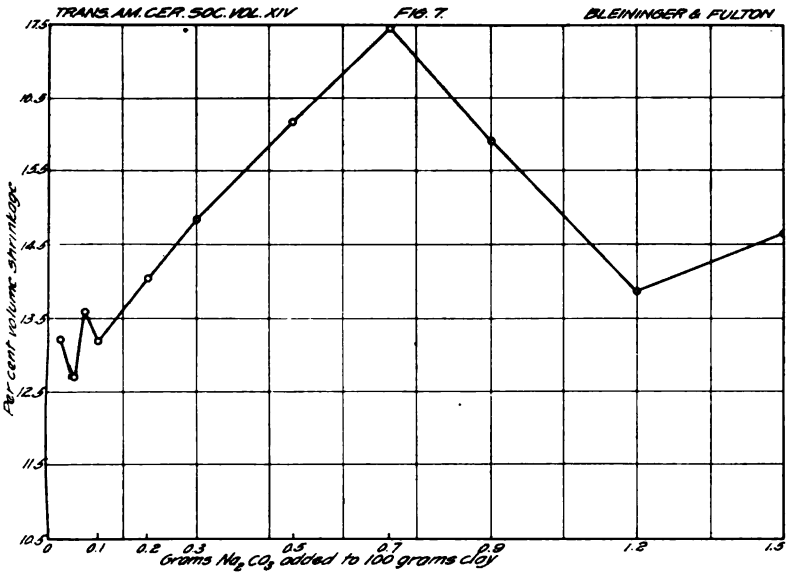

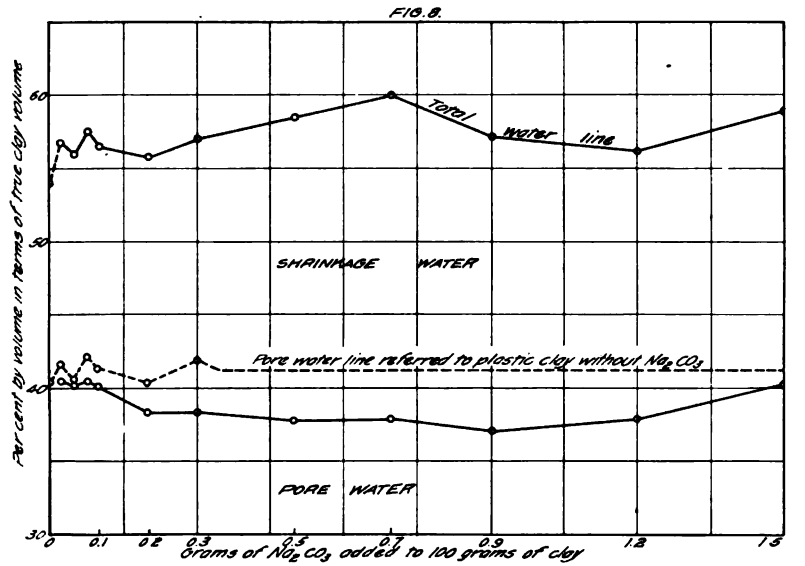

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Similarly, the volume of the total water in terms of the true clay volume is calculated.

In the diagram of Fig. 3, the respective volumes of total and shrinkage water are shown. The boundary between the volumes of water and that of clay is, of course, the line representing zero water and 100 volume per cent. of clay. It is shown in Fig. 3 that the content of pore water has been decreased, that of the shrinkage water having been increased both at the expense of the pore water and due to the rise in the total water content at the two max. points.

The addition of sulphuric acid likewise tends to decrease the shrinkage as is shown in the diagram of Fig. 4.

Effect of Alkalies.—The influence of NaOH is illustrated in the diagram of Fig. 5. It is at once noted that with 0.2 per cent. of this reagent a striking max. point is reached, indicating a marked increase in shrinkage, contrary to what we should expect according to Rohland's views. Only after adding larger amounts does the contraction descend towards the normal value. Here again, according to Fig. 6, the increased shrinkage is due in part to the specific effect of the reagent in increasing the distance between the particles in the plastic state and, in part, to the denser structure of the clay upon drying. Beyond the max. point this condition changes, since the pore water line rises above the normal level. Since, at the same time, the total water line descends, the shrinkage is gradually decreased. The structure of the dried clay is thus more open with the higher contents of NaOH than with the smaller additions.

The growth in shrinkage is still more pronounced in the case of Na_2CO_3, Fig. 7, a phenomenon contrary again to Rohland's statements, although, of course, in this case the effect of the CO_3 ion might have proven a factor, especially if absorption has taken place to any appreciable extent. However, even under this assumption, it is somewhat improbable that the carbonic acid could have brought about such a change where other acids failed to accomplish anything like the same result. In this diagram the maximum occurs with 0.7 per cent. of the reagent. With larger concentrations the shrinkage is again reduced, but appears to gain once more with amounts beyond 1.2 per cent.

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As may be observed from the diagram of Fig. 8, the pore water volume is diminished throughout this series with a gradually increasing total water content up to the maximum.

DEFLOCCULATION SERIES.

It was thought desirable to study the effect of the acids and alkalies upon the clays as regards deflocculation, using solutions of the same concentration present in the plastic clay, as shown by the preceding curves. To illustrate: If to 100 grams of clay, requiring 34.9 per cent. of water, 0.025 gram Na_2CO_3 was added, this would represent a solution carrying $0.025 \div 34.9 = 0.000716$ gram Na_2CO_3 per cubic centimeter of water. Such solutions

Fig. 9.

No.	Wt. clay. Grams	Wt. Na_2CO_3. Grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0	5	...	98	18.0	Clear
1	5	0.0713	98	19.5	"
2	5	0.1423	98	21.8	"
3	5	0.2296	98	24.3	"
4	5	0.4529	98	28.0	"
5	5	0.6803	98	27.4	"
6	5	0.8913	98	28.0	"
7	5	1.0659	98	28.0	"
8	5	1.3549	98	28.0	"
9	5	1.5511	98	28.0	"

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were made up of concentrations corresponding to the various points in the preceding curves. In each case to 5 grams of clay 98 cc. of the solution were added in a graduated tube. The tubes were placed in a shaking machine for 90 minutes and allowed to stand. It was found that the clay itself, without any reagent, settled well, showing a clear, supernatant liquid and a sediment occupying 18 cc.

It was shown that the addition of acid produced no change, excepting in the volume of the sediment, which was finally increased from 18 to 28 cc., as is observed from Fig. 9.

The sodium carbonate solutions, on the other hand, started with conditions of complete deflocculation (Fig. 10). The sediment volumes are shown in the table accompanying each figure.

Fig. 10.

No.	Wt. clay, grams	Wt. Na_2CO_3, grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0	5		98	18	Clear
1	5	0.0702	98	4.5	Very turbid
2	5	0.1426	98	19	Very turbid
3	5	0.2090	98	24	Slightly less turbid
4	5	0.2822	98	24	Less turbid
5	5	0.5713	98	20	Slightly turbid
6	5	0.8388	98	20	Slightly turbid
7	5	1.3642	98	21	Almost clear
8	5	1.8571	98	19	Clear
9	5	2.5059	98	18	Clear
10	5	3.4006	98	18	Clear
11	5	4.0709	98	18	Clear

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The maximum point of the shrinkage curve corresponds to tube No. 8, where the supernatant liquid is clear for the first time.

CONCLUSIONS.

The writers do not attempt at this time to explain the phenomena on theoretical grounds. It is evident that the conditions are quite complex and in order to explain them still further modes of attack must be sought for. The rules laid down by Rohland do not seem to apply, since in the main the acids clearly caused shrinkage to decrease while the alkalies produced the reverse effect, which is contrary to his statements. In order to be fair, however, attention must be called to the fact that shrinkage in this work has been considered a measure of plasticity, while Rohland speaks of plasticity itself without attempting to correlate this property with any numerical value. As is well known, there is at the present time no clear conception as to the relation between plasticity and shrinkage excepting the general fact that the plastic clays as a class show a greater drying shrinkage than the leaner ones.

DISCUSSION.

Mr. R. J. Montgomery: I should like to ask Prof. Bleininger how long those slips in the cylinders had stood when the photographs were taken.

Prof. Bleininger: Twenty-four hours. I might add also that in making the volume determinations they were stored twelve hours in a moist chamber in order to bring about some sort of an equilibrium between the clay and the reagent.

Mr. Kerr: I should like to raise the question as to what determinations, if any, were made of the electrolytes present in the clay before the acids and alkalies were added. Was any general data obtained upon this point?

Prof. Bleininger: No direct determination was, of course, made. However, you have seen the series of tubes which ought to indicate pretty clearly to one familiar with this work whether the initial conditions are acid or alkaline. We are principally endeavoring to get at the experimental facts without much regard to theoretical assumptions. The evidence so far obtained along these lines is not sufficient to base upon it any definite

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line of procedure. The work of Veimarn especially has disturbed previous conclusions by his very startling claims with reference to colloids. We thought it wise to work along the lines which I have indicated.

Mr. Kerr: The only point which I wished to bring up was that if one clay contained positive ions in excess and another clay negative, the addition of either acid or alkali to one clay would not correspond to a similar addition to the other clay. Some clays give a strongly acid reaction, others a weakly acid, while still others are somewhat alkaline. Data upon neutralization might be included.

Prof. Bleininger: This is brought out in the deflocculation experiments. At the same time corrections work very well in theory, but when you come to make them you will find that neutralization does not necessarily follow. I, of course, want to check Mr. Ashley's work in this investigation in a general way. I realize we have learned a good deal from his work and I want to say that he is to be given great credit for having started work of this kind.

Mr. Purdy: I would like to ask if any experiment has been made to determine whether, as a rule, trivalent electrolytes coagulate clays more readily than do the uni- and divalent salts.

Prof. Bleininger: I would say that it has been done with various materials.

Mr. Purdy: Has it been done with clays? I would like to see some experiments tried on that and reported, because I have been unable to show that the trivalent salts have any more effect than the other. That is one of the respects in which the clay is different.

Prof. Bleininger: Mr. Ashley, of course, has done such work.

Mr. Purdy: That is what he did not do, he accused himself on that point.

Prof. Bleininger: I think he did work with phosphates. Of course, as I said before, this work is being continued and we expect to take representative reagents.

Mr. Kerr: What measurements other than volume shrinkage were made?

Prof. Bleininger: We hope to take up various things in

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time. One of them is a vapor tension investigation, for which a special apparatus is now being designed.

Prof. Grout: I would like to ask if the curves which are drawn there, such as the first curve which you show on the screen, were the average of a series of results on one clay or just one series of tests.

Prof. Bleininger: Taken as the average of three determinations in each case.

Prof. Grout: I wondered if that approximation of a maximum was so characteristic that you could report it for publication on one series of tests; whether your area of determination was not such that you might not safely report it.

Prof. Bleininger: Well, we were able to get very good checks, also we notice that the two acids are behaving very similarly. We recognize, however, that there are a good many factors involved which it is almost impossible to correlate in a technical investigation of this kind. Of course, if we were to carry on this investigation from a strictly physical chemical standpoint, we would proceed along somewhat different lines.

Mr. Potts: I would like to ask Prof. Bleininger just what practical application he expects to make of that treatment. Does he propose to make kaolins plastic?

Prof. Bleininger: I haven't any idea as to what this information could be used for and am indifferent in regard to that point.

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NOTE ON TERRA COTTA GLAZES.

By CULLEN W. PARMELEE AND RALPH HEIDINGSFELD.

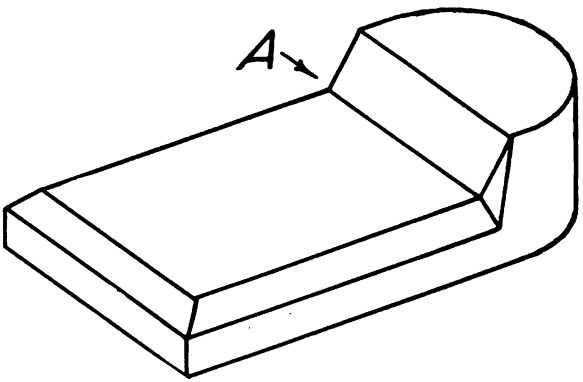
Introduction.—The purpose of the experimental work about to be described was to extend the field of investigation over those glazes which are of the Bristol type but made somewhat more complex because of the introduction of magnesium and barium in addition to the ordinary bases, lime, zinc and potash.

Materials.—The raw materials used for the glaze composition were: feldspar, Golding Sons Co., whiting, zinc oxide, Edgar's Florida clay, flint, heavy magnesium carbonate, barium carbonate.

Preparation of Samples.—The glazes were prepared by weighing out the extremes, grinding them wet in a ball mill for one hour and screening. These extremes were blended for intermediates according to the usual method. A good check on the accuracy of the weighing and blending was had by the fact that certain of the glazes in each series were repeated in other series for which other weighings were made.

The glazes were applied by spraying upon unburned terra cotta body trials which had been coated with an underslip. The trial pieces were made by pressing the plastic body in plaster molds. The body was of the following mixture:

50 per cent. Raritan Ridge No. 33 50 per cent. Edgar's No. 9	70 per cent.
Fine grog	30 per cent.



Trial piece.

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The form of the trial pieces used was as shown in the sketch. This form has the advantage of offering a plane surface met by another plane surface at an angle (A), which will be referred to hereafter as the bevel angle. This angle affords an excellent test of the power of the glaze to flow smoothly and cover surfaces having raised ornaments. Many glazes which cover plane surfaces faultlessly fail to give satisfaction on ornamented surfaces. When the angle was not properly closed but presented a broken surface contact, the appearance of the crack was useful also in the formation of an opinion as to the relative fusibility of the glazes under observation. The plane surfaces of the trials were generally free from "crawling," although occasionally small cracks designated as "surface cracks" appeared. These were generally an eighth of an inch or so in length. Sometimes these appeared in the shape of the letter Y. It is probably true that some of these imperfections were due to some slight fault in the application which could be prevented by a little more care. All the spraying of underslip and glazes was done by one person, and we have reason to believe that it was quite uniformly done.

The trials were set on edge in saggers and fired in a laboratory kiln to cone 6 in 18 hours. Our practice was to raise the temperature fairly rapidly to within a hundred degrees or less of the proper temperature, then hold it as nearly constant as practicable for 3 hours or more and slowly bring down the desired cone. The results of these burns were checked by selecting the best of our series for burns in commercial kilns. The results of the laboratory burns have thus been confirmed.

VARIATION OF RO.

The first portion of the work undertaken was to vary the members of the RO group, keeping the alumina and silica constant as follows:

$$RO\ 0.56\ Al_2O_3,\ 3.08\ SiO_2.$$

For the convenience which a graphic presentation always possesses, we arranged our series in such a manner as to have one or two constant members, leaving three variables. This we found could be plotted readily upon a triaxial diagram. This arrangement is easily understood by examining the accompanying diagrams.

The results obtained are indicated in Figs. 1 to 7.

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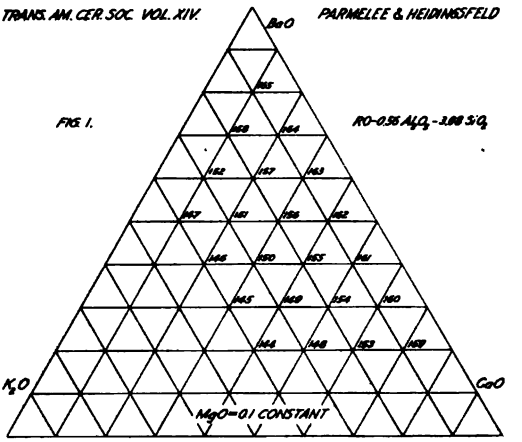
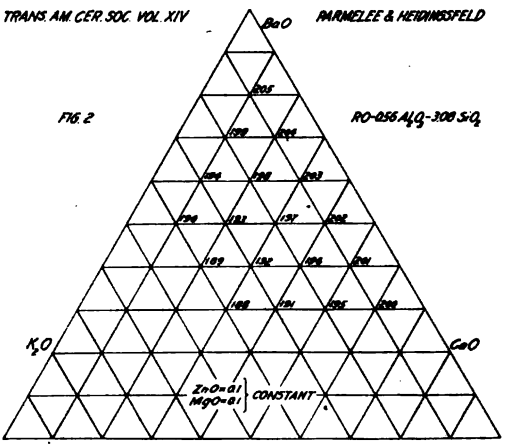


These glazes would be better if fired higher. The best are 144, 145 and 148, which have matured well, are dull and have good surface. All the other glazes are immature. Those having high barium are hardly vitrified.



Number 188 was partly matte and partly bubbled. Another burn gave a glossy glaze having a good surface, but containing many fine bubbles. Number 189 was partly matte and partly bubbled as was also 190. Numbers 195 and 200 were immature.

The following were merely vitreous: 192, 193, 196, 197, 201, 202.

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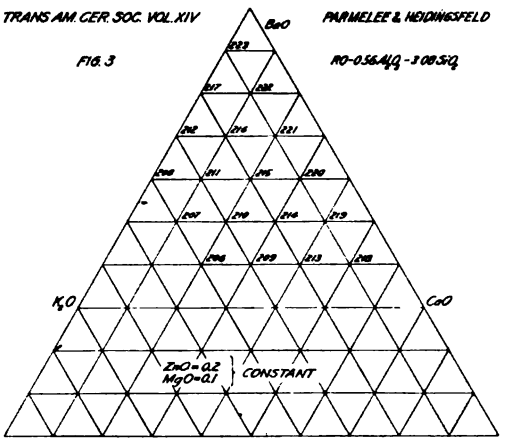
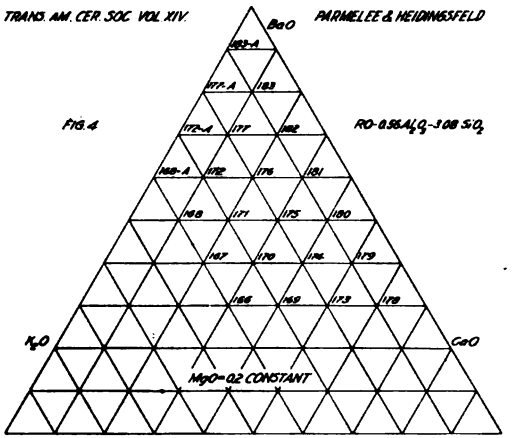


Number 206, glossy and with good surface. Number 207, not matured. Number 209, dull matte. Number 210, immature matte. Vitreous slips: 211, 216, 215, 221, 220.



The best matured are 166 and 169, which are dull or matte. They are too refractory to fuse well and the surfaces are wavy.

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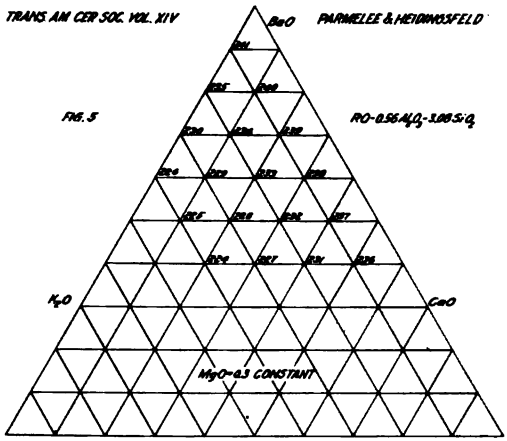
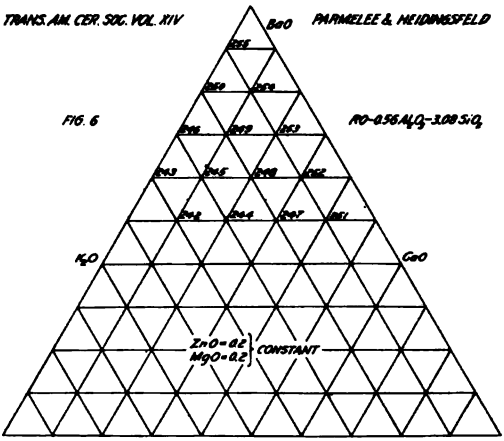


None matured. Are scarcely vitreous in appearance.



Number 242 has a dull or matte surface, which is not well matured. There are many pin-holes. Number 244 is less matured.

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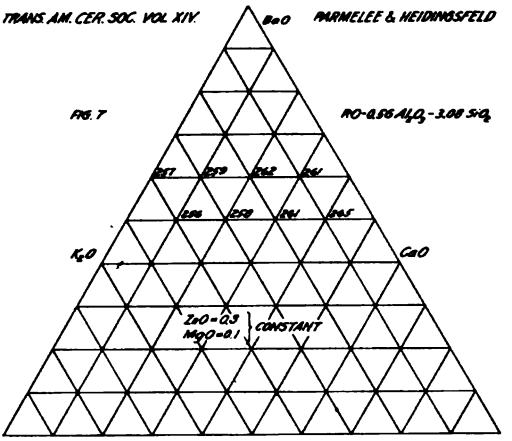

Number 256 has glossy surface, containing many pin-holes. Number 258 is similar.

VARIATION OF SILICA AND ALUMINA.

Selecting from the foregoing experiments the most promising RO groups, we chose the following for further experiments:

FORMULAE OF RO.

MgO.	BaO	K_2O	CaO	ZnO	MgO	BaO	K_2O	CaO	ZnO
0.1	0.1	0.4	0.4	...	0.1	0.1	0.3	0.5	...
0.1	0.1	0.4	0.3	0.1	0.2	0.1	0.3	0.4	...
0.1	0.1	0.4	0.2	0.2	0.1	0.1	0.3	0.3	0.2
0.1	0.1	0.4	0.1	0.3	0.1	0.1	0.3	0.2	0.3
0.2	0.1	0.4	0.1	0.2	0.1	0.1	0.3	0.1	0.4
0.2	0.1	0.4	0.3	...	0.1	0.1	0.5	0.3	...
0.3	0.1	0.4	0.2	...	0.1	0.1	0.5	0.2	0.1
0.1	0.2	0.4	0.3	...	0.1	0.1	0.5	0.1	0.2
0.1	0.2	0.4	0.1	0.2	0.2	0.1	0.3	0.1	0.3

With these RO groups we varied the alumina and silica content as follows:

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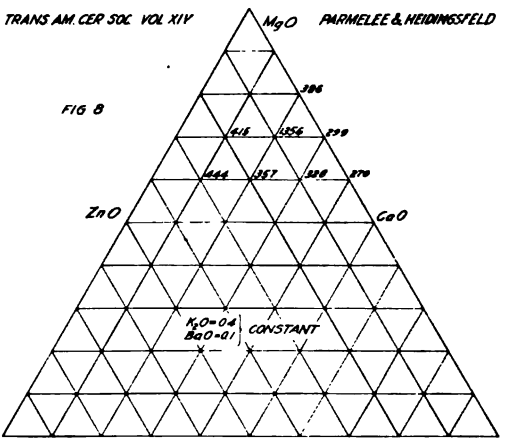
Equiv. of Al_2O_3	Alumina-Silica Ratio. 1 : 5	1 : 6	1 : 7	1 : 8	1 : 9
	Equivalents of Silica.				
0.4	2.0	2.4	2.8	3.20	3.60
0.45	2.25	2.70	3.15	3.60	4.05
0.50	2.5	3.00	3.50	4.00	4.50
0.55	2.75	3.30	3.85	4.40	4.95
0.60	3.00	3.60	4.20	4.80	5.40
0.65	3.25	3.90	4.55	5.20	5.85
0.70	3.50	4.20	4.90	5.60	6.30
0.80	4.00	4.80	5.60	6.40	7.20

In some instances it was impracticable to make all the variations shown.

The accompanying Figs. 8, 9 and 10 show the positions of the RO members chosen for experiments.

Results of this Series.—The results obtained with these glazes are the same as have been observed with ordinary lime-zinc-potash or Bristol glazes. The whiteness and consequent opacity increases with the increase in the zinc content. With this increase of zinc, we find also higher gloss and a larger number of surface defects, such as cracks large and small. When high zinc is used a low alumina content is advisable since a better maturity is had. High zinc content with high alumina and silica gives a surface that is either pitted badly or bubbled.



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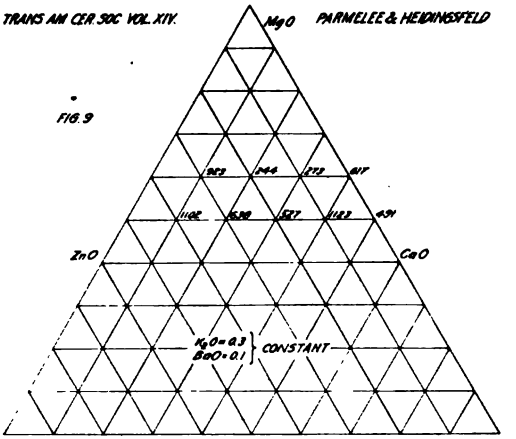

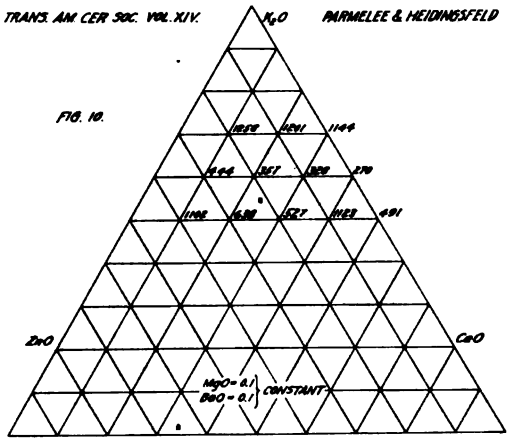

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A high lime content tends to give dull or matte glazes. If the alumina content is 0.65 equivalent, then a high lime content gives immaturity. None of the high lime glazes gave opacity comparable with that obtained with zinc.

Magnesia had a marked influence upon the fusibility of the glazes. Those having 0.3 equivalent of magnesia did not mature. The series containing no zinc and 0.2 MgO did not mature as well as one containing 0.2 ZnO, both containing the same amount of K_2O. An increase of the zinc to 0.3 equivalent did not improve the glaze. The presence of magnesia in glazes not containing zinc seemed to slightly increase the opacity. The effect was not noticeable in those containing zinc.

The increase in the amount of potash increased the fusibility of the glazes. This was more apparent in comparing glazes high in zinc than those of high lime content. Such increase of opacity as was noticed was of the nature of a milky translucency rather than the white opacity due to high zinc.

An increase of barium decreased the fusibility, but not to the same degree as was effected by increase of magnesia.

The best alumina content, or at least one which always gave as good results as were obtained in any series, was 0.55 equivalent. The most satisfactory alumina-silica ratio was 1 : 5 or 1 : 6. It was found that, with the combinations of RO members experimented with, a considerable variation in alumina and in the alumina-silica ratios could be had.

Crazing was not observed in glazes which had been sprayed on our own underslip and body except when the trial kiln had been opened and the samples drawn while hot. Then we found that those having more than 0.1 equivalent of magnesia and more than 0.2 zinc oxide crazed, the potash being constant at 0.4 equivalent and the barium at 0.1 equivalent. An increase of the clay content decreased crazing in these cases. None of the trials using our body and slip and burned in a commercial kiln have crazed.

The best matteness was observed on trials having RO groups high in lime, low in alumina and silica. An increase of silica resulted in a higher gloss and in many instances an increased fusibility. This was much more evident with some RO groups than with others.

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THE MELTING POINTS OF PYROMETRIC CONES UNDER VARIOUS CONDITIONS.

By SAMUEL GEIJSBEEK, Portland, Oregon.

INTRODUCTION.

The measurements of high temperatures is a study in which we still find many contradictory results. In the many tests and experiments made by various investigators, it has been shown that only those instruments which use a thermo-couple have given accurate temperature readings at the time of observation. The optical instruments have given only fairly good results, but as the eye is the only agent of observation, the readings taken by such instruments may vary accordingly.

In a paper read by the author before this Society in 1904, regarding the fusion points of Seger cones expressed in degrees,[1] it was pointed out that pyrometric cones do not always melt at the same temperature, and that they will melt at lower temperatures than the published tables, which are furnished by cone manufacturers, show. These temperatures vary according to the length of time of the burning period. A pyrometric cone will melt at a higher temperature the shorter the duration of the burning period, so that in test kilns the published data regarding their melting temperatures is nearly correct, for the burning tests are always of short duration, from 15 minutes up to a few hours. The longer the time of burning the lower will be the actual temperature at which pyrometric cones will melt.

On account of the published tables of the melting points of pyrometric cones, many contradictory statements have been made by clayworkers regarding the actual temperatures employed in burning their kilns. Several instances can be traced where statements thus made have not aided the scientific side of clayworking engineering. In one instance, a gas-fired kiln was built with a guarantee that the clay would vitrify at a certain temperature, which specified also a certain number of pyrometric cones corresponding to this temperature. The kiln was built properly, and after it had been fired sufficient to make the guarantee good, it was found when the guaranteed temperature

[1] Trans A. C. S., Vol. VI, p. 94.

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was obtained as measured with a pyrometer, the corresponding cones were already melted long before this period of guaranteed temperature. The reverse was also observed that if the kiln was fired according to the pyrometric cones as mentioned in the guarantee, the guaranteed temperature was never obtained. Upon investigation, it was found that the experiments with clays to be burnt in this kiln, and upon which the guarantees were based, were made in a small test kiln, and therefore the temperatures did not check when applied to a large commercial kiln. The tests were made with a thermo-couple and cones and there the temperatures checked all right. The concern having this trouble is still in legal difficulties over the discrepancy in temperature measurements between cones and actual temperatures.

HOFFMAN'S REPORT.

Having investigated this matter closely, it was gratifying to the writer to note that the German clayworkers took steps to rectify the erroneous idea regarding the actual melting points of Seger cones. The matter was taken up about two years ago with the Imperial Government, and the investigations were assigned to the Imperial Physical Technical Testing Station, located in Berlin.

At the last annual meeting of the German Association of Fire Clay Manufacturers, Dr. Hoffmann reported[2] the results of the investigations of the Imperial Government regarding the behavior of the Seger cones under fire. The request for these investigations was made by this association. The report is given here only as to the main points. Dr. Hoffmann states:

"As many objections were made in regard to the temperatures of the melting points of cones as stated in the circulars which the cone manufacturers distribute among their customers, experiments were made to establish the correctness of these objections. The obtained results show plainly that the objections were fully warranted and justified. Already in former years there had been observed a difference between the actual temperature readings of cones melting in large or small kilns, and between short and long fires. The previous tests were conducted at the Royal Prussian Porcelain factory, while the tests this year were conducted at the Bendorfer factory of the Rheinish Chamotte and Dinas Works. The temperature of the melt-

[2] Tonindustrie Zeitung, 1911, p. 1099.

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ing points of Seger cones 4–35 was already formerly established by pyrometer measurement in an iridium test kiln.[3]

The first observations on a commercial kiln were made by the German Imperial Testing Station in 1906 at the Oest Chamotte Works in Wittenberg. It was here demonstrated that Seger cone 14, which melted down in an experimental kiln at 1410° C. (2570° F.), melted in this kiln far below that point. These experiments were continued in February, 1910, at the Royal Prussian Porcelain factory with two different kilns and with Seger cones 7–14. The temperatures were measured with a platinum-platinum rhodium element and a recording galvonometer, and also with an optical Holborn-Kurlbaum pyrometer. The readings of these two types of pyrometers were nearly alike, but the melting points of the Seger cones were considerably below these printed on the circulars and of which data has been prepared on the iridium kiln test.

The difference for Seger cones 7 and 8 was about 200° F., while for Seger cone 13 it was about 144°, and for Seger cone 14 about 75° F. It was also observed that after cone 13 had melted, the heat had to be raised about 100° before cone 14 was melted, while the difference should be only 36° between cones.

In the experiments at Bensdorf, Seger cones 2 to 17 were used. One test was conducted in a Dinas brick kiln, while the other one was made with a round downdraft kiln for burning fire brick. The thermo-couples were so arranged that they nearly touched the cones. The cones were considered down when the point touched the bottom of the fire clay slab on which they were standing. In the Dinas brick kiln two sets of cones and pyrometers were used to check the results.

Table I.—Table of Different Melting Temperatures of Seger Cones 2-17 in Degrees Fahrenheit according to Dr. Hoffman.

Number of cones	Temperature according to circulars	Actual melting temperatures		
		In electric furnace	In porcelain kiln	In firebrick kiln
2.....	2138	..	..	2057
3.....	2174	..	..	2093
4.....	2210	2237	..	2120
5.....	2246	2237	..	..
6.....	2282	2300	..	below
7.....	2318	2345	2156	2200
8.....	2354	2381	2174	2210
9.....	2390	2435	2237	2219
10.....	2426	2451	2237	2264
13.....	2534	2543	2399	..
14.....	2570	2579	2507	..
16.....	2642	2660	..	2543
17.....	2678	2696	..	2552

[3] Tonindustrie Zeitung, 1907, p. 1366, and 1909, p. 1577.

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The obtained results indicate that Seger cones will melt at an earlier period and at a lower point in all commercial ceramic kilns than in test kilns, and the temperatures as tabulated by the Imperial Testing Station have, therefore, no value for practical purposes.

Dr. Hoffmann states further that there are many causes for these differences, and thinks that the kiln gases exercise a chemical action on the cones, but as these questions are not within the scope of the work of the Testing Station, they have not been investigated.

In conclusion, it was stated that the work of the Imperial Testing Station, so far as the melting points of cones 4–35 was concerned, was finished. It has been proven that Seger cones are not stable enough to express in degrees of heat the temperature of commercial ceramic kilns, and should, therefore, not be used in the determination of the actual temperatures of such kilns. When a difference of over 180 degrees Fahrenheit has been observed between the same cones in two kilns, while in another kiln under similar conditions the difference was only 20 degrees for the same cones, there is sufficient grounds that cones are not reliable as far as actual melting points are concerned. If for some reason or another, the temperature of a kiln must be taken, it will always be advisable to make use of a pyrometer which has proven to give accurate readings. In all cases, however, where it is only a question of controlling the burning process, Seger cones can be used to advantage, but no attention should be paid to their melting points as expressed in degrees of temperature.

RIEKE'S WORK.

Dr. R. Rieke, in a series of articles in Sprechsaal[4] touching the melting points of Seger cones 022–15, states that it is only natural that artificial mixtures, like pyrometric cones, which are made up from the different oxides, carbonates and silicates, do not have a distinct melting point like the metals or other chemical combinations. This point has been brought out so

[4] Sprechsaal, Nos. 50–51, 1911.

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often that it is rather surprising that we still continue to compare the melting points of the Seger cones with degrees of heat expressed either in Fahrenheit or Centigrade temperature scales, which have *a constant value*. It is therefore only natural that such comparisons have brought out severe criticism regarding the actual melting points of Seger cones.

The melting of Seger cones is a process which depends upon a number of different changes which gradually take place in the course of firing. The course of the process does not indicate any absolute temperature to be measured at any stage of the firing period, but gives a good, reliable comparison of the melting points of different materials, if made always under the same conditions.

The different changes to which clays and bodies are subjected under fire are identically the same as the changes which take place in the melting of Seger cones, and therefore a comparison between the melting process of both is proper, provided the firing conditions are the same. Objection should be raised, therefore, to a comparison between a burning test and its results made in a small laboratory furnace or kiln and similar tests made in a large commercial furnace or kiln, for in these tests the firing conditions are not the same.

It is a well known fact that clays and ceramic bodies show a great difference in regard to their shrinkage, porosity, transparency and vitrification when they are burnt in a small laboratory kiln or burnt in a large commercial kiln, even if the actual temperature as recorded by a pyrometer has been the same in both instances. This difference can be traced to the action of the silicates which is different according to the duration of the burning process. There are some other differences which should also be taken into account; but as they do not apply as much to Seger cones mixtures, they will be left untouched.

The work which Dr. Rieke undertook was the determination of the melting points of Seger cones 022–15 in different kilns and to consider the following three points:

"First.—If the melting points of the Seger cones would be the same in the same kiln, under as near as possible the same burning conditions regarding the quickness of the heating and burning process.

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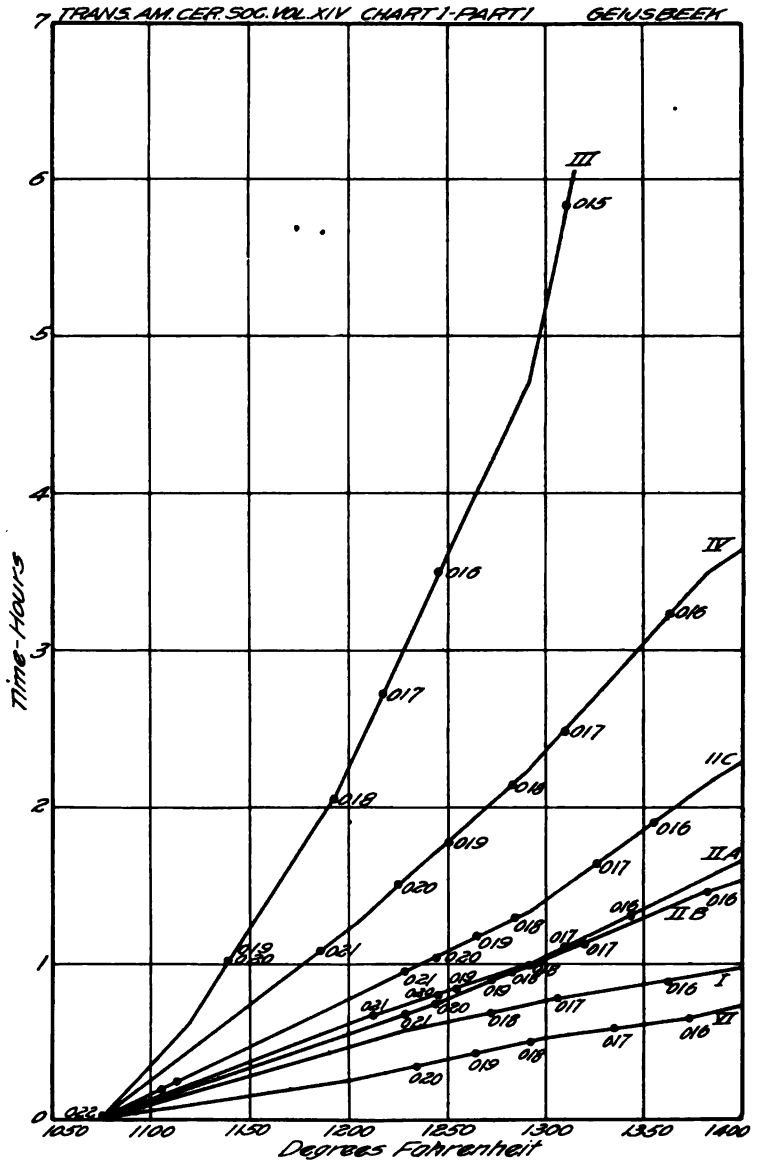

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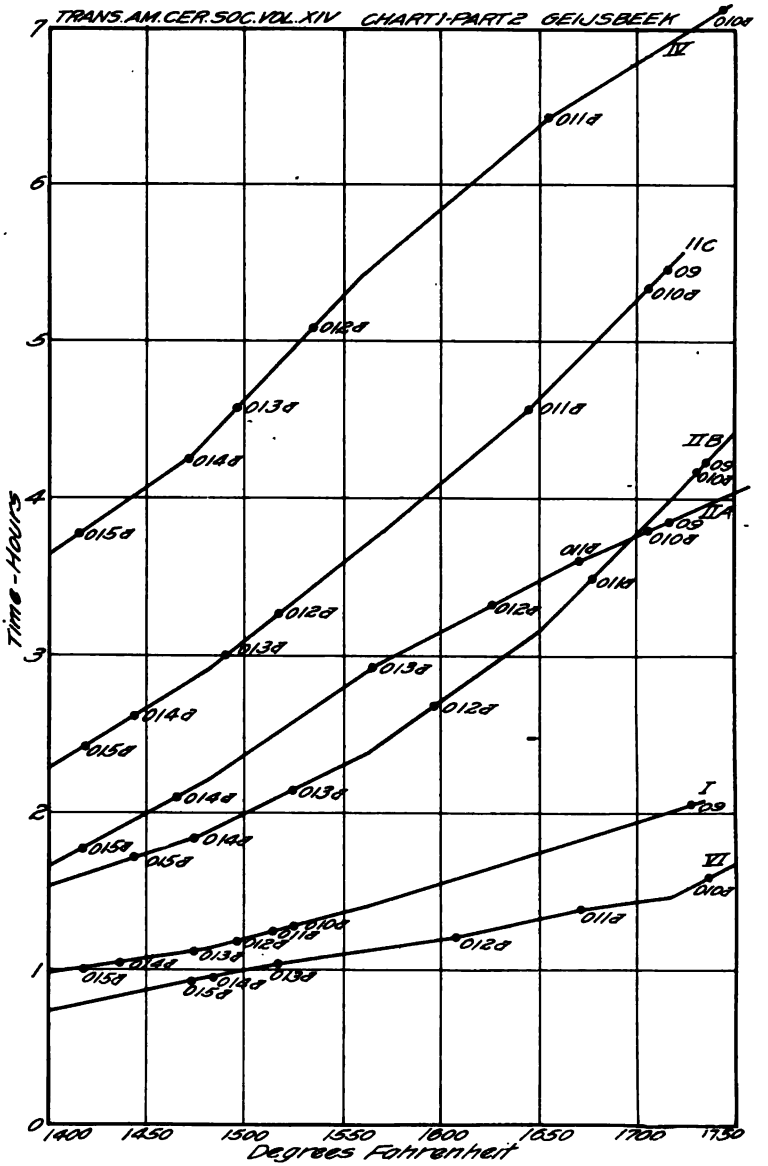

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"Second.—How great the difference is in the melting point of Seger cones in different kilns?

"Third.—To what causes can these differences be traced?

"The Seger cones used in these tests were divided into five groups, and each group consisted of the following cones·

"Group 1. The lowest numbers of the series from cones 022–016 which were made according to the formulas of Dr. Simonis.[5]

"Group 2. New Seger cones 015*a*–011*a* which do not compare either in composition nor melting point with the old cones 015–011.

"Group 3. The old Seger cones of 010–6.

"Group 4. The new Seger cones of series 010*a*–6*a* as introduced into the trade in 1908.

"Group 5. The cones 7–15, which were made according to the standard Seger formulas."

The temperatures were measured with a platinum-platinum rhodium thermo-couple, placed so that the end of the couple was as near to the cones as possible.

TESTS OF GROUPS 1 and 2.

As the melting of these cones is very close, the two groups are combined in this one burning test. They were tested in six different kilns:

Kiln I, muffle kiln of 8.8 cubic feet content, fired with wood.

Kiln II, muffle kiln of 17.6 cubic feet content, fired with wood.

Kiln III, biscuit kiln of a soft porcelain kiln, fired with wood.

Kiln IV, biscuit kiln of a hard porcelain kiln, fired with coal.

Kiln V, biscuit kiln of a hard porcelain kiln, fired with wood.

Kiln VI, Heraeus electric kiln.

The results of these tests are shown in Chart I. This illustrates the relative position of the melting points of the cones. The ordinates are the hours of the duration of the tests, while the abscissae are marked in degrees Fahrenheit. The actual temperatures as measured with the pyrometer are given in Table II in degrees Fahrenheit:

[5] Sprechsaal, No. 41, 1908. Keramische Rundschau, Nos. 42 and 43, 1908. Tonindustrie Zeitung, No. 119, 1908.

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Table II.—Table of Different Melting Points of Seger Cones 022 to 09 according to Dr. Rieke.[6]

Number of cones	Temperature according to circulars	Actual melting temperatures.							
		Kiln I	Kiln II			Kiln III	Kiln IV	Kiln V	Kiln VI
			Test A	Test B	Test C				
022	1094	..	1112	1112	1103	1076	..	..	..
021	1148	..	1211	1230	1230	..	1184	..	..
020	1202	..	1247	1247	1247	1139	1229	..	1238
019	1256	..	1256	1274	1265	1139	..	..	1265
018	1310	1274	1292	1292	1283	1193	1283	..	1292
017	1364	1319	1310	1328	1328	1238	1310	..	1337
016	1418	1364	1346	1382	1355	1247	1364	..	1373
015a	1472	1418	1418	1445	1418	1319	1418	..	1472
014a	1526	1436	1463	1472	1445	..	1472	..	1481
013a	1580	1472	1562	1526	1490	..	1499	..	1517
012a	1634	1499	1625	1598	1517	..	1535	1580	1607
011a	1688	1517	1670	1679	1643	..	..	1661	1670
010a	1742	1526	1706	1733	1706	..	1742	1715	1733
09	1778	1724	1715	1733	1715	1742	1742	..	..

The length of time it took to raise the temperature from 1112 degrees to 1724 degrees Fahrenheit was in

Kiln II, Test A, 3 hours and 47 minutes.
Kiln II, Test B, 3 hours and 49 minutes.
Kiln II, Test C, 5 hours and 10 minutes.
Kiln IV, 6 hours and 52 minutes.

To raise the temperature in Kiln I from 1202 to 1724 it took 1 hour and 33 minutes, while in Kiln III it took 4 hours and 10 minutes to gain a temperature from 1112 to 1292. The electric kiln, VI, was heated at the rate of from 5 to 7 degrees every minute.

In examining Table II closely we find that Seger cones 022–021–020 have a higher melting temperature than listed, while all other cones have a lower one. The greatest difference is in Seger cone 021 which shows +96 degrees, while it is the lowest in Seger cone 019 with —17 degrees. While the Seger cones should have an exact difference of 54 degrees as stated in the circulars of the

[6] Chart 1, showing the temperature curves and the relative melting points, goes with this table.

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cone manufacturers, only six cones in these two series come near to this space, while all others are either lower or higher. The smallest difference is between cones 021 and 022 with 10 degrees, while the greatest difference is between cone 012 and 011 with 73 degrees. That the Seger cones will melt at lower temperature as the rate of firing is slower is characteristically indicated in test on Kiln III, where with a very slow fire the melting point of the cones was very much lower than in other cases.

Seger cones 016 and 015 melted fairly regularly, but cones 013*a*–011*a* will melt with quick fire at lower temperatures, while just the opposite was observed with cone 022–016.

In order to check some of these tests, it was arranged to fire the electric furnace very slowly, and the duration is indicated in the following table:

To raise from	1112 to 1202	degrees it took	4	hours
"	1202 to 1292	"	1	hour
"	1292 to 1382	"	2	hours
"	1382 to 1472	"	5	"
"	1472 to 1562	"	2½	"
"	1562 to 1652	"	2	"
"	1652 to 1724	"	1	hour

It thus took 17½ hours to raise this temperature from 1112 to 1724 degrees, and the cones showed the following melting points:

Cone 016	1319	degrees Fahrenheit
015*a*	1364	"
014*a*	1373	"
013*a*	1607	"
012*a*	1634	"
011*a*	1706	"

This checks fairly well with the temperatures obtained in commercial ceramic kilns.

TESTS OF GROUP 3.

In this group the old Seger cones from 010 to 6 were tested. The course of this group should be particularly observed as these cones are still in use at present, in spite of the fact that there are cones of the new series with corresponding numbers on the market also. The melting points of these two series are not alike,

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neither are their compositions. The old cones from 010 to 3 were mixed with iron oxide, while the new ones, which are called 010*a* to 6*a*, do not contain any iron oxides.

The test of these cones were conducted in the following kilns:

Kiln VII, soft porcelain kiln, 44 cubic feet content, fired with wood.

Kiln VIII, soft porcelain kiln, 212 cubic feet content, fired with wood.

Kiln IX, hard porcelain kiln, 635 cubic feet content, fired with coal.

Kiln X, hard porcelain kiln, 176 cubic feet content, fired with wood.

Kiln VI, Heraeus electric kiln as used before.

Table III gives the actual temperatures at which the cones of this group melted in the different kilns, while the temperature curves are shown in Chart 2.

Table III.—Table of Different Melting Points of Seger Cones 010—6, Old Series.[7]

Number of Cones	Temperature according to circulars	Actual melting temperatures.									
		Kiln VII		Kiln VIII				Kiln IX	Kiln X		Kiln VI
		Test A.	Test B	Test A	Test B	Test C	Test D		Test A	Test B	
010	1742	1751	1706	1751	..	..	..	..	..	..	.
09	1778	1778	1778	1778	1796	1760	..	1742	1742	1688	..
08	1814	1868	1832	1859	1859	1832	..	..	..	1742	1877
07	1850	1940	1913	1931	1895	1913	..	..	..	1796	1904
06	1886	1967	..	1958	1967	1931	..	..	..	1868	1958
05	1922	1994	1967	1994	2003	1949	1922	1976	1904	1922	2003
04	1958	2021	2030	1994	2003	2030	1940	..	..	1958	2039
03	1994	..	..	2030	2021	2048	2003	..	..	1976	2056
02	2030	2057	2075	2057	2075	..	2012	..	..	2003	2066
01	2066	2111	2120	2084	2093	..	2012	..	2012	2012	2084
1	2102	2111	..	2111	2093	..	2021	2129	2012	2030	2102
2	2138	2111	..	2102	2093	2093	2066	2129	2030	2039	..
3	2174	2111	2147	..	2102	2102	2102	2156	..	2075	..
4	2210	2165	2165	2138	2120	2120	2120	2174	2084	2093	..
5	2246	..	..	2147	2129	2120	2129	2183	..	2120	..
6	2282	..	..	2165	2138	..	2129	2201	2129	2129	..

[7] Chart No. II, showing the temperature curves and the melting points, goes with this table.

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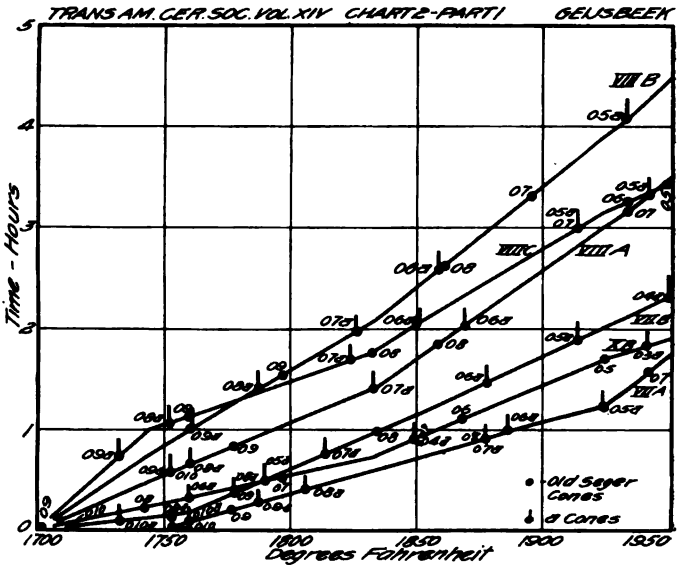

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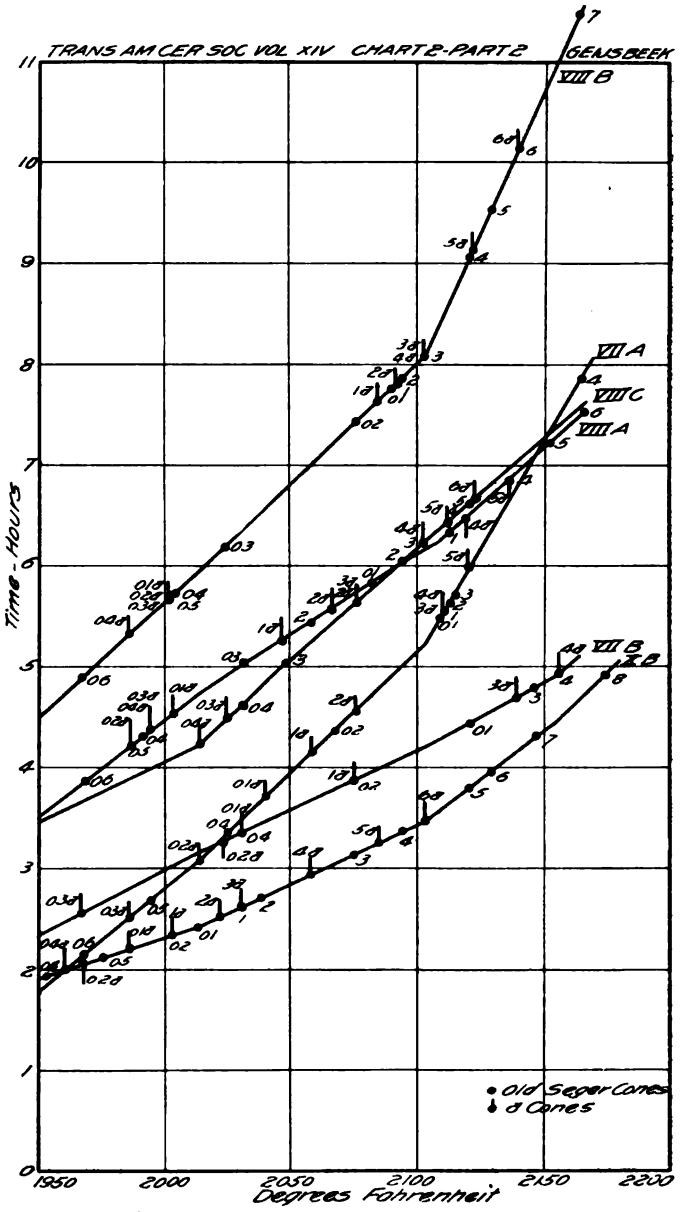

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Table IV.—Table Showing Rate of Firing and Raising Temperature in Minutes for Results as Shown in Table III.

Temperature raise in degrees F.	Kiln VII		Kiln VIII				Kiln IX.	Kiln X	
	Test A	Test B	Test A	Test B	Test C	Test D		Test A	Test B
1742-1832	38	60	55	80	50	...	15	...	30
1832-1922	40	60	95	110	80	50	15	85	60
1922-2012	110	70	105	120	65	75	15	80	40
2012-2102	125	65	85	130	120	60	15	75	65
2102-2156	135	40	70	180	130	125	9	100	60
Total Temperature Raise in Total Time in Hours									
1742-2156	7.28	4.45	6.50	10.20	7.25	5.10	1.9	5.40	4.15

Some Seger cones show a great difference, ranging from 70 to 150 degrees. The exact cause of these differences is rather hard to determine. It has been brought out in these investigations that those cones which contain iron oxide are subject to change by kiln gases, and that the formation of iron silicates will produce lower melting points. The same observations which were made in the cones of Groups 1 and 2 were also found to exist in Group 3. The volatilization of the boracic acid in these cones will raise their melting point, and this is especially true of the Seger cones 010–01. The outer parts of these cones will become poorer in boracic acid than the inside, and in consequence will fuse at higher heat. This can be observed very often in the melted cones. The action of boracic acid will also help the crystallization of the silicates, especially when the temperature has been raised slowly in the early stages of the firing. This has been observed in those cones which have been heard for a long time below their melting point, and such cones will eventually melt at higher temperatures above their melting point. A cone on which the edges and top are still sharp but where the inside is smoothly molten is a good illustration of this case.

Cones 010 and 09 will melt for these same reasons in a muffle kiln with quick fire at lower temperature than in a glost fire of a porcelain kiln, and a difference of between 50 and 80 degrees has been observed. In the slow fire of a biscuit kiln, these cones have melted at 150 degrees higher than in a muffle kiln. An

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exception in this case are the cones in Kiln X, test B, as here the temperature was raised quicker than in any other burning test.

The close melting points of cones 05 and 04 in Kiln VIII, tests A and B, can be traced to the same cause. In these tests the temperature remained constant for a long time around the melting point of cone 05, so that the next cone started to melt also, and both went down together when the temperature rose just a little.

Cones 1 to 3 behave somewhat similar to cones 010–01, but they do not act as quick as there is no boracic acid present. The melting points in the higher number cones, all above cone 4, are again different from the other ones. The fluxes decrease more and more, and the alumina and silica content are greater in proportion. The viscosity of silicates which have only a little alumina demands not only a higher temperature but also a slower raise in temperature. The silicates will soften quicker by long fire and low temperature than by quick fire and high temperature.

In the tests of the biscuit kilns, it was found further that cones which have been biscuited will melt at higher temperature than new cones. The difference is about one cone, and in some cases it amounts to two cones.

GROUP 4. NEW CONES 010a-6a.

These new cones,[8] which were introduced in 1908, have a difference in their qualitative composition from the old ones. Cones 010*a*–3*a* have no iron oxide, and, further, all cones have magnesite. These *a*-cones have the great advantage that on account of the fact that they do not have any iron content, they are less sensitive to the kiln gases.

The trouble with iron in the old cones was already pointed out in 1900 by Gorton.[9] He made up a series of cones with more boracic acid at the expense of the silica and eliminating the iron content. Cones made from these series of mixtures gave none of the trouble experienced in the use of the cones containing iron. After some experimenting Hottinger[10] reached the following con-

[8] Sprechsaal, No. 41, 1098, p. 561.
[9] Trans. A. C. S., Vol. II, p. 60.
[10] Trans. A. C. S., Vol. III, p. 183.

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clusions regarding these old cones: That in the cones from 010 to 01 or those in which a boro-silicate is used, the oxide of iron introduces an element of uncertainty into the mixtures which is unnecessary and that the iron can well be dropped. Further, that the oxide of iron is not in itself the cause of the irregularities in the behavior of these lower cones, when used in muffle terra cotta kilns. That the real causes of the difficulties is the volatilization of boracic acid from the cones by the action of the sulphuric acid of the fuel gases and also the changing of calcium carbonate into sulphate. Hottinger advises the use of some other frit for the making of these lower cones, which is not so readily attacked by the acid vapors.

Simonis aimed to get a greater difference or gap between the melting point and the rate of firing in constructing these new series of cones. The results of the tests show, however, that he succeeded only partially, and they also tend to impress the fact that it is impossible to compound with the materials at our disposal in the ceramic industries mixtures which will have their melting points entirely independent of the duration of the firing.

Table V.—Table of Different Melting Points of New Cones 010a-6a Series.[11]

Number of cones	Temperature according to circulars	Actual melting temperatures.										
		Kiln VII		Kiln VIII					Kiln IX	Kiln X		Kiln VI
		Test A	Test B	Test A	Test B	Test C	Test D			Test A	Test B	
010a	1652	1760	1733	1670	..	..	..		..	1670	..	1733
09a	1688	1778	1751	1751	1760	1733	..		..	..	..	1769
08a	1724	1805	1778	1760	1787	1751	..		..	..	1688	1796
07a	1760	..	1814	1832	1823	1823	..		..	..	1724	1832
06a	1796	1886	1877	1868	1859	1850	..		..	..	1760	1859
05a	1832	1922	1913	1940	1931	1913	..		..	..	1787	1931
04a	1868	1958	1949	1994	1985	2012	1886		..	..	1850	1940
03a	1904	1985	1967	1994	2003	2021	1940		..	..	1940	1967
02a	1940	2012	2021	1985	2003	..	2012		..	..	1967	1994
01a	1976	2039	2030	2003	2003	..	..		..	1976	1985	2048
1a	2012	2057	2075	2057	2084	..	2030		..	2030	2003	2075
2a	2048	2075	..	2066	2093	2075	2048		2084	..	2021	.
3a	2084	2111	2138	..	2102	2075	2066		2120	2066	2030	.
4a	2120	2111	2156	2129	2102	2102	2102		2138	2093	2057	..
5a	2156	2120	..	2138	2120	2111	2102		2174	..	2084	..
6a	2192	..	..	2174	2138	2120	2120		2183	2129	2102	..

[11] Chart 2 also shows the melting points and curves of this series.

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The results of tests are shown in Table V, and the temperature curve and the melting point are shown on Chart 2.

The tests were made in the same kilns as mentioned in Group 3, and the duration of the firing was the same as shown in Table IV. The results readily show the same relation to exist in these new cones as in the old ones. The main cause of the different melting point is here also the duration of the firing. When the temperatures in the kilns are nearly constant or only increase a few degrees, the succeeding cones will nearly all melt at the same temperature as shown in Table V in Kiln VII, test A, between cones 3*a* and 5*a*, further in Kiln VIII, test A, between cones 04*a* and 01*a*, and in same kiln in test B between cones 03*a* and 01*a*, and 1*a* and 4*a*.

In order to test these obtained temperatures, the cones of this group were also tested in an electric kiln, which was heated so that the temperature was raised from 7–9 degrees per minute, and the results are also shown in Table V. Further, the cones were biscuited and then tested, and the same difference as stated above was found to exist in these cones also.

GROUP 5. CONES 5 TO 17.

As the cones in this group were about identical with the ones used in the tests made by Dr. Hoffmann, the results of these two tests were compared, and it was found that with slow firing

Table VI.—Table of Different Melting Points of Seger Cones 6-15.

Number of cones	Temperature according to circulars	Actual melting temperatures					
		Kiln VIII		Kiln IX		Kiln X.	Kiln XI
		Test B	Test C	Test A	Test B	Test A	
6	2192	2120	2129	2201	..	2129	..
7	2246	2129	2156	2228	..	2147	2228
8	2282	2210	..	2264	2264	2174	2264
9	2336	2264	..	2327	2345	2246	2300
10	2372	2300	..	..	..	2255	2336
11	2408	2318	..	..	2372	2318	2372
12	2462	..	..	..	2444	2336	..
13	2516	..	..	2417	2507	2363	..
14	2570	..	..	2534	2579	2426	2498
15	2615	..	..	2570	2588	..	2570

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the temperatures were nearly alike; but when the cones were fired in the quick heat of a porcelain kiln, there was some 100 degrees difference in the cones from 4 to 12.

The same kilns were used as before, and the results are shown in Table VI. Kiln XI is a hard porcelain kiln, fired with wood, of about 635 cubic feet content.

In order to check the slow firing heats, and to ascertain if the very slow and long duration of the firing exercise such great action on the cones, the electric kiln was heated up to a certain temperature, and then fired very slowly. Cones 5*a*, 6*a*, 6, 7, 8, and 9 were tested. They were heated in the electric kiln to 2084 degrees in one hour, and then the temperature was held constant between 2084 and 2102 degrees. In $1^3/_4$ hours, cone 5*a* melted, and $1^3/_4$ hours afterwards cone 6*a* went down. The heat was kept up for ½ hour longer and then stopped; cone 6 was just bending.

In another trial cones 6–10 were heated for a long time between 1100 and 1180 degrees. After this temperature was held for 45 minutes, cone 6 started to bend and was completely melted down in one hour and 30 minutes. Forty-five minutes after that, cone 7 melted, and 15 minutes later cone 8 went down. Three hours later cone 9 started to melt. These tests show conclusively that it is possible without raising the temperature to melt cones 5*a*, 6*a*, 6, 7, and 8, in rapid succession through the action of long period of firing only and at a temperature which is 225 degrees lower than Dr. Hoffmann obtained in his iridium furnace.

CONCLUSIONS.

The results of the tests made regarding the melting points of Seger cones, which have been cited here, are of great value to the clayworking industries. Inasmuch as the cones are made from the identical materials that we use in the clayworking line, it must be conceded that a great deal of the trouble which we have in order to obtain uniform results in burning our ware can be traced to the long or short duration of the firing and to the action of the kiln gases. Every burner is familiar with the fact that a soaking heat will burn his ware harder, even if the temperature does not increase; further, that it is very hard work

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to raise the temperature after it once has been stationary at a soaking heat, and also that the quick firing of any kiln of ware will produce entirely different results from slow firing.

In order to know exactly therefore at what rate of firing we are burning our kilns, it is imperative that we should take constantly temperature measurements with a recording or indicating pyrometer, so that we can ascertain if the heat is raised slowly or quickly, or if the heat is a soaking one. By keeping such temperature records, we then know the rate of firing which has been given the burning of a kiln, and only with such records are we able to duplicate results.

In conclusion of the data presented above, it can be stated:

First. That Seger or pyrometric cones are very sensitive in their melting according to a slow or quick fire and that they will melt at a lower temperature in a long duration of firing than in a quick fire.

Second. That Seger or pyrometric cones will melt down at approximately the same temperatures in the same kiln, if used under the same conditions.

Third. That cones which are used once, and which are therefore biscuited, are of no value for further use, as they give no corresponding results with new cones.

Fourth. That the difference or rate of increase between the melting point of each cone and its succeeding number is not constant and will vary in some cones more than in others.

Fifth. That Seger or pyrometric cones cannot be used to determine exact temperatures as their melting points are subjected to various changes, and therefore any data furnished showing their melting point expressed in degrees of heat is problematical.

DISCUSSION.

NOTE SUBMITTED AFTER READING THE PAPER.

Professor Orton: Mr. Geijsbeek has made a very good résumé of the matter which has been published concerning the melting of Seger cones. He has made no new points, so far as the writer can see, but his paper has value, nevertheless, from the fact that it makes available the results of articles which have been

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locked up heretofore in the German journals and therefore not available to more than a few American clayworkers.

The writer, and every one else who has given the subject attention, agrees that Seger cones, or any similar series of prepared silicate mixtures, cannot be used for the accurate determination of temperatures. It is generally conceded that it was unfortunate that Dr. Seger, in first introducing the cones, brought in the idea of using them for measuring temperatures, and there are grounds for believing that Dr. Seger recognized this himself shortly after it had been done. There was more excuse for it then than now, however, for pyrometers were then but little used and expensive, while in the last 20 years several kinds of them have been widely exploited commercially and are within the reach of anyone who has a need to measure high temperatures accurately.

Unfortunate as it is that the use of a printed scale of temperatures was ever started in connection with cones, it is also true that the confusion which would ensue if the idea of temperature were wholly abandoned would be worse than the trouble now existing. Anyone who uses cones regularly for a little while soon learns to use the cones by number, and forgets all about their supposed melting points in the thermometric scale. The beginner, who knows nothing of cones, naturally starts with the other conception, but his experience soon broadens his view and shows him wherein the real values of the cone lies.

The value of the pyrometric cone system devised by Dr. Seger and extended by Cremer, Hecht, Simonis and others, and imitated more or less openly in the Holdcroft bars sold in England, lies in the fact that it does something which no mere measurement of temperature by itself, or no measurement of time and temperature together, can do. As Mr. Geijsbeek has pointed out, the vitrification of a piece of clayware and the melting of a cone are strictly comparable processes. The factors which control one are the same that control the other. Time and temperature are only two of these factors. Some of the more important remaining are: (*a*) The proportion of the various minerals composing the mixture; (*b*) their condition, as to freshness or partial alteration by weathering; (*c*) their condition as to fine-

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ness of grain; (*d*) their condition as to homogeneity of mixture; (*e*) the rate of increase of the temperature changes; (*f*) the duration of periods when the temperature remains fixed; (*g*) the percentage of oxygen, or the percentage of reducing gases in the kiln atmosphere; (*h*) the percentage of sulphuric or sulphurous acid gas in the kiln atmosphere; (*i*) the density or compactness of the silicate structure; (*j*) the pressure to which it is subject while vitrifying; and probably several others. Every clay or other silicate which vitrifies, or melts, is affected by all of these influences, and its fusion is in one sense the algebraic sum of all these influences, some working for and some against the process. It follows that the best and safest index of the rate at which a silicate is vitrifying or melting is a method which itself is affected by the same variables.

There are some other processes in use which seek to accomplish the same result by other means, *viz.*, by measurement of shrinkage, or volume changes. The old Wedgewood pyrometer of nearly 150 years ago is now being re-introduced in improved form, and used as a guide for the rate of progress of vitrification. Shrinkage measurements by brick-makers, by use of the "settling rod," are known to all clayworkers. Encaustic tile makers and electric porcelain makers have long been accustomed to carefully caliper their trial pieces and determine how the process is going on by the volume change. These methods are all of value, for the same reason that cones are.

The last twenty years cover the entire life history of high temperature pyrometers as commercial tools. During this time, they have been greatly simplified and improved, and brought within the reach of all so far as price is concerned. During this time a half dozen or more firms in this country with skilful salesmen have been competing eagerly to introduce them into all industries where high temperatures are used; and they have been of incalculable service in rendering these industries accurate and sytematic, where heretofore they were much affected by chance or factors not under control.

It is certainly not a mere coincidence, however, that during this same period the use of the cone system, or some more or less complete equivalent for it, has grown rapidly and steadily in all

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countries where accurate ceramic engineering is practiced. In America, it has been introduced almost wholly without the use of advertising methods or the use of salesmen, yet the use of cones has attained large proportions and still continues to steadily increase. Many of the largest users of cones have, meanwhile, installed one or other of the pyrometer systems, and find benefit from their use; but the pyrometer very seldom replaces the use of the cones or trial pieces, or any of the old and well known methods of measuring kiln conditions. They are added to what was being done before.

The fact of the matter is that only in a few places can the reading of any pyrometer, no matter how accurate, be taken as the final criterion of a heat treatment. In no ceramic industry should it be so used. In silicate fusions or vitrification, we need all the help we can get from any source, and no wise manufacturer neglects any method which will make his results more sure. One cannot know too much of what is transpiring in a kiln of claywares at the "settling heat."

The only criticism which the writer desires to make of Mr. Geijsbeek's article is that in dwelling so strongly upon the disabilities of the cone system as to its thermometric functions, which every interested party cheerfully concedes in advance, and saying so little of its advantages as a measure of the process of vitrification of silicates, he might unwittingly create the impression in the minds of beginners that the cone system is a dangerous thing or clayworkers to use and that it should be replaced by the recording pyrometers. It seems to the writer that the fair-minded attitude is to criticize every system for its faults and failings, and commend it for what good it possesses, and finally, to encourage every clayworker to make use of every aid that all the systems can give him in carrying out his difficult and hazardous task of clay-burning.

Mr. Geijsbeek: The remarks of Prof. Orton will certainly make it plain that the circulars which are distributed by him in the sale of pyrometric cones are misleading to a certain extent inasmuch as they show tables in which cone numbers are given in one column, degrees centigrade in a second column and degrees Fahrenheit in a third column. I trust that when he prints a

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new edition of such circulars he will do away with such tables as he now states plainly that cones have no accurate melting point in the thermometric scale. This would help not only the beginners but would make it easier for clayworkers in general to make better comparison between a pyrometric temperature value and the melting points of cones. Since we have gathered such a great mass of evidence as presented in my article, it is evident that cone manufacturers will in the future present better data regarding the melting point of pyrometric cones.

It has never come to my mind to criticize the usefulness of cones, as it is a well known fact that I was among the first clayworkers in this country to advocate their use in all clayworking plants, and this was at the time that Prof Orton held the following opinion of the usefulness of Seger cones as stated in his report on the "Clayworking Industries of Ohio" (Geol. Sur. of Ohio, Vol. VII, pub. 1893): "This system of Seger cones is ingenious and to potters who are in possession of all material and machinery for making the mixtures as well as the knowledge of the principles of fluxing involved, it is possible that this idea may be useful, but for the clayworker in the commoner forms, it is not likely to find any extended field ofusefulness." We are certainly glad that the author of this expression has changed his mind, and has given us facilities for the purchasing of pyrometric cones in this country.

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